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THE CORROSION OF POWER PLANT EQUIPMENT BY FLUE GASES

A REPORT OF AN INVESTIGATION

CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS

IN COÖPERATION WITH

THE UTILITIES RESEARCH COMMISSION

BY

HENRY FRASER JOHNSTONE

BULLETIN No. 228

ENGINEERING EXPERIMENT STATION

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THE CORROSION OF POWER PLANT EQUIPMENT BY FLUE GASES

I. Introduction

1. *Preliminary Statement.*—This bulletin is a report of an investigation carried on in the Engineering Experiment Station of the University of Illinois in coöperative agreement with the Utilities Research Commission of Chicago. The Commission is composed of representatives of the following companies: Chicago North Shore and Milwaukee Railroad Company, Chicago Rapid Transit Company, Commonwealth Edison Company, Middle West Utilities Company, Midland United Company, Public Service Company of Northern Illinois, and The Peoples Gas Light and Coke Company.

The officers of the Commission are: Mr. W. L. Abbott, Chairman; Mr. J. L. Hecht, Mr. R. B. Harper, Mr. Samuel Insull, Jr., Vice Chairmen; Mr. G. W. Williamson, Treasurer; Mr. H. B. Gear, Secretary; and Mr. Wm. A. Durgin, Director. The advisory subcommittee directing the work of this investigation is composed of Mr. A. D. Bailey, Superintendent of Generating Stations, Commonwealth Edison Company, Chairman; Mr. A. J. Authenrieth, Vice President, Ice Department, Middle West Utilities Company; Mr. A. E. Grunert, Efficiency Engineer, Generating Stations, Commonwealth Edison Company; Mr. R. B. Harper, Chief Testing Engineer, The Peoples Gas Light and Coke Company; Mr. J. M. Lee, Assistant to the Vice President, Public Service Company of Northern Illinois; and Mr. E. Mandel, Chemical Engineer, Testing Department, Commonwealth Edison Company.

2. *Scope of Problem.*—The developments which have taken place in the design and operation of central power stations in the last decade have been far-reaching. The increased efficiency resulting from the integration of control and facilities offers many advantages that cannot be obtained otherwise. The attainment of higher steam temperatures and pressures, higher boiler ratings, longer hours of operation, and lower flue gas temperatures, have greatly decreased the cost of production. At the same time, however, the supply of high grade coal has been ever diminishing. At present the trend in plant operation, especially in the mid-continental area, is toward the use of lower grade coals in the large power stations where equipment can be assembled to burn it efficiently, leaving the better but more expensive fuel for domestic appliances, smaller industrial furnaces, and metal-

lurgical processes. This development, of course, has been timely, since industry in general must sooner or later make use of the poorer types of coal. Among the problems that have arisen as a result of the innovations is that of the effect of the combustion products on the equipment. The simultaneous decrease in the exit gas temperatures and the increase in the sulphur content of the coal, as well as a change in the character of the ash, have produced a condition most favorable for corrosion. As a result of these modifications, the deterioration in the economizers and preheaters, especially at temperatures where the metal may exist below the dew-point of the gases, is quite severe. The use of higher operating pressures has also entered into the development of the problem because of the greater prevalence of leaks, a condition which also is favorable to rapid corrosion. In some cases the corrosion has been so severe that the life of a preheater tube is not greater than one year and failures in the colder section of the economizer have taken place in as short a time as three months. With continued developments in the general direction outlined, this corrosion may be expected to become more and more severe unless some step is taken to prevent it. It was with this object in mind that the Research Commission suggested the problem to the Engineering Experiment Station as one of great importance.

The investigation so far has been of a technical nature and no attempt has been made to try out new features of operation under plant conditions. It has been the general object first to find out what the factors are that are contributing most to the corrosion, and then to study methods of their elimination or the prevention by some other means. This bulletin describes the conditions which are prevalent in flue gases that cause corrosion and some of the steps that may be taken towards their elimination. The reactions that take place in a boiler furnace are discussed and their effect on corrosion and slag formation are brought out. A description of the experimental work carried on in the laboratory on corrosion and its results will also be given. These substantiate the ideas of the cause of the corrosion suggested by the plant data. The results of tests on various corrosion-resisting alloys and protective coatings under the conditions existing in the flue gases are reported. A description is also given of new methods for the determination of the dew-point and sulphur dioxide and trioxide concentrations in flue gases. Finally, a discussion of the fundamental corrosion reactions is made in order that the work reported here may be carried forward by others who may be interested in this field.

3. *Acknowledgments.*—The investigation was conducted under the supervision of DEAN M. S. KETCHUM, the Director of the Engineering Experiment Station, and of PROF. D. B. KEYES, Head of the Division of Industrial Chemistry. The writer wishes to express his appreciation to Professor Keyes for his kind suggestions and criticisms concerning the work.

Thanks are also extended to PROF. S. W. PARR, Emeritus Professor of Applied Chemistry; to DR. DANA BURKS, JR., Special Research Assistant Professor in the Engineering Experiment Station; and to MR. F. B. HOBART, formerly on the staff of the Experiment Station, for their interest and suggestions which have materially aided the progress of the investigation.

Much information concerning the plant conditions has been furnished by outside companies. Especial coöperation has been given by the TESTING and EFFICIENCY DEPARTMENTS of the COMMONWEALTH EDISON COMPANY of Chicago, Illinois, and by the operating staff at the WAUKEGAN GENERATING STATION at Waukegan, Illinois. MR. H. F. RUTH, chemist for the OHIO POWER COMPANY at Philo, Ohio, has been active in collecting and furnishing data that have been useful in the investigation. Other companies which have furnished data are: THE BABCOCK AND WILCOX COMPANY, THE BIGELOW COMPANY, and the UNITED GAS IMPROVEMENT COMPANY. Various manufacturers have furnished data on the corrosion of different types of alloys.

II. CONDITIONS PREVALENT IN FLUE GASES CAUSING CORROSION

A. Data from Power Plants

4. *Survey of Plants.*—In order to determine definitely what factors present in furnace gases may be regarded as those controlling the rate of corrosion, a survey was made of several power stations operating in various sections of the United States. Included in the investigation were both plants experiencing corrosion from the combustion products and those which have been practically free from this trouble. In many cases plants were visited and the economizers and preheaters closely inspected for localized and general corrosion. Conditions of operation and characteristics of design also were ascertained. In all cases the operating staffs furnished data that were useful in summarizing the conditions that would favor corrosion.

The information obtained is summarized in Tables 1 to 3. The plants are designated by letters so that a comparison of the charac-

TABLE 1
BOILER ROOM EQUIPMENT

Plant	Firing		Boiler					Economizer					Preheater	
	Method	Type	Type	Pressure lb. per sq. in.	Area Heating Surface sq. ft.	Ratio Furnace Vol. to Heating Surface	Furnace Walls Cooling	Type	Construction	Material	Area Heating Surface sq. ft.	Cleaning	Type	Area Heating Surface sq. ft.
A	Stoker	Chain	Cross-drum	700	16 600 17 300	0.34 0.36	Air and Water	Return bend	Horizontal	Steel	7 000 10 250	Washing	Plate and Tube	10 000 18 000
B	Stoker	Chain	Cross-drum	285	15 000	0.30	Refrac.	Rolled Joint	Horizontal	Steel	9 660	Washing	None	None
C	Stoker	Chain	Cross-drum	650	21 500	0.35		Ret. bd.	Horizontal	Cu-Mo Steel	16 000	Washing	Plate	12 000 51 000
D	Stoker	Under-feed	Bigelow	285	14 600	0.62	Refrac.	Ro. jt.	Vertical	Steel	3 500	Washing	None	None
E	Stoker	Chain	Cross-drum	385	15 000	0.41	Water	Ro. jt.	Horizontal	Steel	7 560 10 692	Soot-blowers	Plate	11 750 13 700
F	Stoker	Chain	Stirling	225	6 900	0.21	Refrac.	Sectional	Horizontal	Cast iron		Scrapers	None	None
G	Stoker	Under-feed	Stirling	345	12 000	0.57	Refrac.	Ro. jt.-Fin tube	Ver. and Horizontal	Steel	3 000 5 900		None	None
H	Stoker	Chain	Cross-drum	700	14 100	0.30 0.43	Refrac. and Water	Ro. jt.	Horizontal	Steel	8 800	Steam and Washing	Tube	11 125
I	Oil, Gas Pulverized Coke	....	Cross-drum	650	13 800	1.22	Water	Ret. bd.	Horizontal	Steel	9 800	None	Plate	32 800
J	Pulverized	....	Cross-drum	375	6 000	2.06	Refrac. and Water	Ro. jt.	Horizontal	Steel	8 850	Steam	Tube	41 700
K	Pulverized	....	Stirling	390	29 000	0.83	Air	Ro. jt.	Horizontal	Steel	18 900	Steam	None	None
L	Pulverized	....	Cross-drum	625	15 100	0.80	Air	Ro. jt.	Horizontal	Steel	7 300	.....	Tube	9 900
M	Pulverized	....	Cross-drum	350	18 000	0.65 0.75	Air and Water	.....	None	....	.....	.....	Plate	11 700
N	Pulverized and Stoker	Under-feed	Cross-drum	275	27 200 22 900	0.62 0.33	Air and Water	.....	None	....	.....	.....	Plate and Rotary	13 000
O	Stoker and gas	Chain	Cross-drum	260	12 600	0.32	Refrac.	.....	Vertical	Cast iron	8 250	Scrapers	None	None

TABLE 2
AVERAGE OPERATING CONDITIONS

Plant	Boiler		Economizer					Preheater		
	Evaporation 1000 lb. per hr.	Steam Temp. deg. F.	CO_2 in Gases per cent	Temp. Gas In deg. F.	Temp. Gas Out deg. F.	Temp. Water In deg. F.	Temp. Water Out deg. F.	Temp. Gas In deg. F.	Temp. Gas Out deg. F.	Temp. Air Out deg. F.
A	100–140	675	11–13	580	370	300	390	370	290	220
B	100	640	11–13	520	320	205	280	...	...	...
C	75–130	700	11.5–12	585	340	200	350	340	240	175
D	95–110	580	12–13	550	460	195	250	...	...	...
E	.....	...	13	550	325	205	305	325	270	220
F	35	675	12–14	...	...	150	...	...	...	...
G	90	660	12–13.5	670	350	235	335	...	...	...
H	100–125	700	12–13	650	420	240	330	420	235	300
I	250	750	10–10.5	770	510	285	375	510	370	370
J	200	660	13–15	1050	350	205	425	350	230	380
K	350	700	14.5	535	280	200	312	...	...	...
L	100–140	722	13–15	650	350	210	328	350	270	260
M	125	715	13–15	...	...	...	...	545	360	275
N	200–250	610	13–14	...	...	...	...	475	390	217
O	90	600	12	544	322	177	269	...	...	...

TABLE 3
FUEL USED IN POWER PLANTS*

Plant	Seam	Location of Mines	Proximate Analysis				Ultimate Analysis						
			Moisture per cent	Ash per cent	Fixed Carbon per cent	Volatile per cent	C per cent	H per cent	O per cent	N per cent	S per cent	B. t. u.	Fusion Point of Ash deg. F.
A	Ill. No. 6	Christian Co., Ill.	14.5	14.1	37.8	33.6	55.6	3.86	7.01	1.13	4.45	10 100	1990
B	Ill. No. 6	Christian Co., Ill.	14.5	14.1	37.8	33.6	55.6	3.86	7.01	1.13	4.45	10 100	1990
C	Middle Kittaning	Muskingum Co., O.	9.2	11.7	43.5	35.6	67.7	5.22	11.82	1.40	3.18	11 280	2000
D	Pittsburgh	Pennsylvania	7.4	9.7	45.5	37.3	65.4	4.50	8.24	1.23	3.33	12 124	2066
E	Mystic	Iowa	20.0	18.9	32.4	28.7	48.1	3.47	5.92	0.98	5.0	8 664	1950
F	Pittsburgh No. 8	Ohio	5.5	11.1	46.0	37.4	66.9	4.25	6.62	1.13	3.4	12 290	2100
G	Cherokee	Crawford Co., Kan.	9.6	13.7	46.1	29.9	63.2	3.74	6.21	1.10	3.9	11 200	1950
H	Ill. No. 6	Williamson Co., Ill.	13.2	9.2	48.7	33.8	63.9	4.33	6.22	1.33	2.1	11 450	2200
I†													
J	Ill. No. 6	Christian Co., Ill.	10.5	14.9	39.6	35.2	58.2	4.04	7.35	1.18	4.67	10 500	1990
K		W. Va. and Ky.	1.3	7.5	59.3	33.2	77.1	5.28	6.46	1.38	1.07	13 900	2400 or higher
L		Logan Co., W. Va.	1.0	8.0	59.5	33.2	77.6	5.14	6.33	1.36	0.58	13 900	2710
M	Ill. No. 6	Jackson Co., Ill.	8.0	15.3	45.7	31.0	62.5	4.14	7.27	1.38	1.47	10 910	2210
N		Allegheny Co., Pa.	2.4	10.2	53.5	33.8	72.9	4.87	6.03	1.52	1.40	13 475	2200
O		Logan Co., W. Va.	1.1	9.7	55.4	34.2	79.0	4.37	4.88	1.21	0.80	13 500	2900

*All percentages reported on "as received" basis.
†Petroleum residues and natural gas—see p. 28.

teristics of design, conditions of operation, and type of fuel used may be made. In Table 1 is shown the equipment used at the various plants, while Table 2 is a summary of the operating conditions. The characteristics of the fuel used are included in Table 3.

Besides the survey of these power plants, an investigation was made of the prevalence of corrosion from the flue gases encountered in waste-heat boilers of gas plants, and in oil heaters in petroleum refineries. The conditions of temperature and moisture should be similar in these cases to those found in furnace gases resulting from the combustion of coal.

5. *Summary of Plant Data.*—The results of these surveys may be summarized as follows:

(1) Corrosion is most often present when the sulphur content of the coal is above 2 per cent. No instances of corrosion were found when the sulphur content was below this value. High sulphur coal does not always produce corrosion, however, even when the operating conditions are similar to those in plants where corrosion is prevalent.

(2) Corrosion in pulverized fuel systems is never severe, even when the same fuel produces corrosion when fired on a stoker.

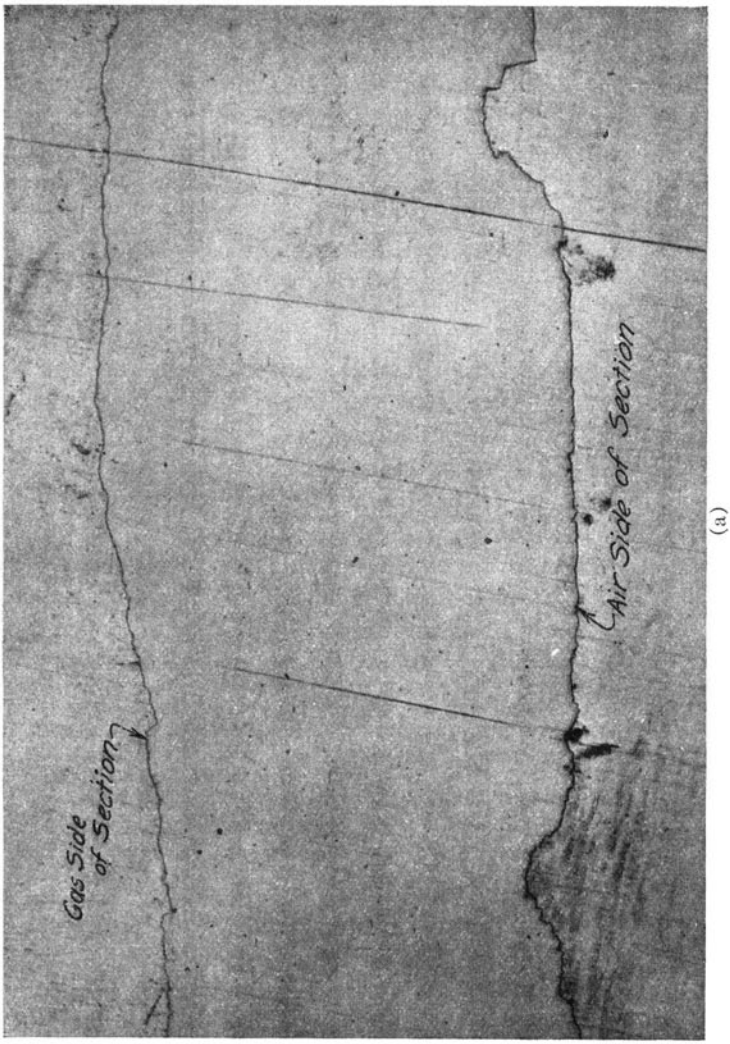
(3) Corrosion is most prevalent from high ash coals and under those conditions of operation in which a high draft is employed, so that a great deal of flue dust is carried up by the gases. In many cases where corrosion is severe, trouble is also experienced from the slagging of the boiler tubes.

(4) The zone of maximum corrosion is usually that immediately in front of the air intake on the air preheater.

(5) The highest metal temperature at which severe corrosion is encountered is about 300 deg. F. Above this temperature the slight corrosion is similar in extent and in type to that which takes place on ordinary boiler tubes.

(6) The corrosion of preheater tubes is aided by the erosive action of the ash particles. It is significant that under the microscope the corroded cross-sectional edges of preheater tubes have a smooth outline while those of the economizer tubes are rough and pitted (Figs. 1 and 2).

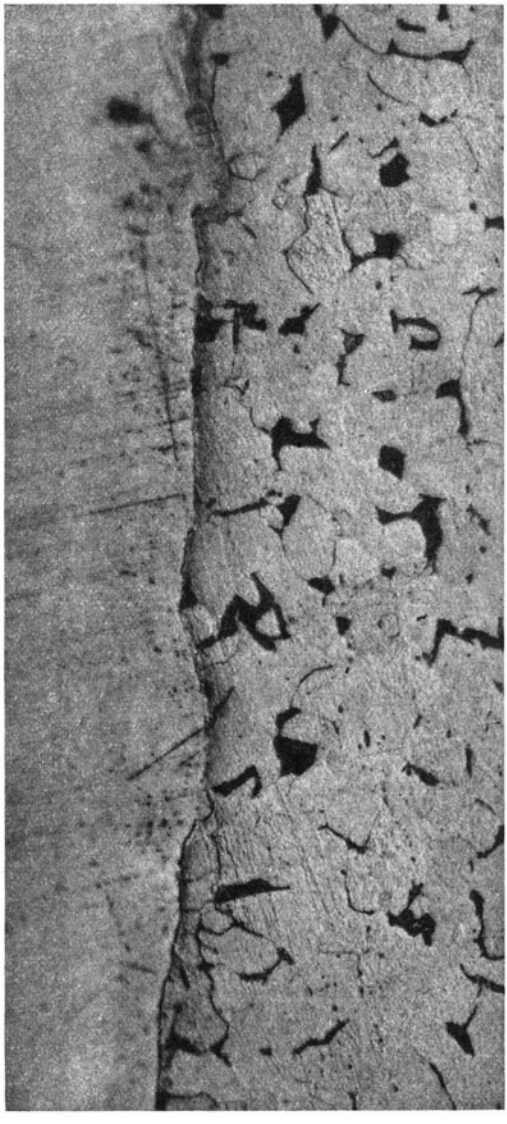
(7) The presence of a zone of high moisture, caused either by a leak or by a steam soot blower, will produce corrosion by the gases from almost any type of coal. This localized corrosion takes place at points in the neighborhood of the escaping steam (Fig. 3) and is distinct from the erosive action of a direct steam-water jet (Fig. 4).



(a)

Unetched (x150).
Upper edge is the corroded edge (gas side); lower edge is the air side.
Note absence of pits in corroded edge.

FIG. 1. MICROGRAPHS OF CROSS-SECTION OF CORRODED PREHEATER TUBE



(b)

Etched, 2 per cent Nital (x200).
Same as upper edge in (a).

FIG. 1 (CONTINUED). MICROGRAPHS OF CROSS-SECTION OF CORRODED PREHEATER TUBE
Specimens were copper-plated to prevent "rolling" during polishing.

FIG. 2. MICROGRAPH OF CORRODED ECONOMIZER TUBE

Etched, 2 per cent Nital (x150).

Note prevalence of pits. This specimen was cut from the center of a tube where only general corrosion could occur. Copper plating was used here, also, to protect the edge during polishing.

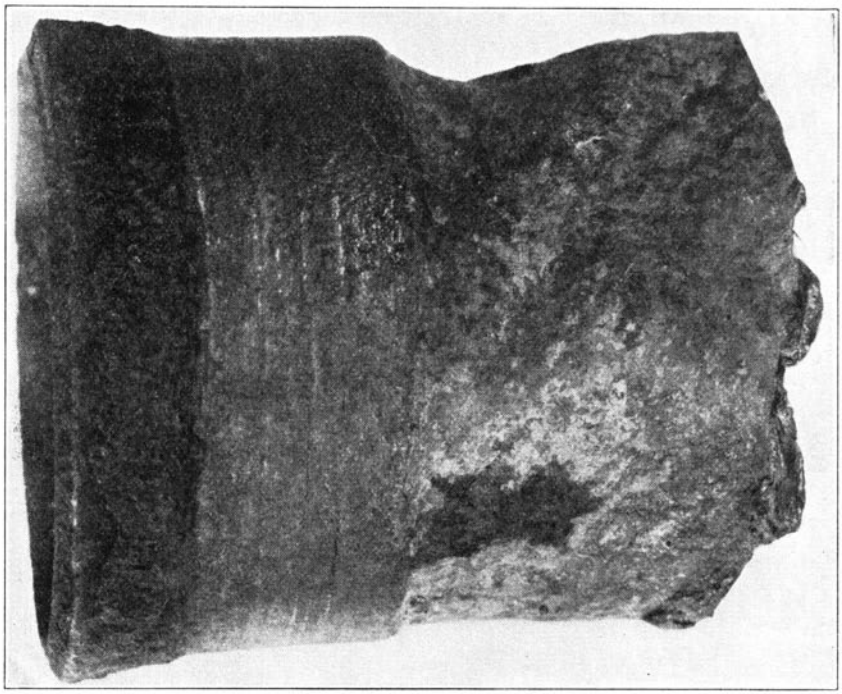


FIG. 3. LOCAL CORROSION CAUSED BY A LEAK

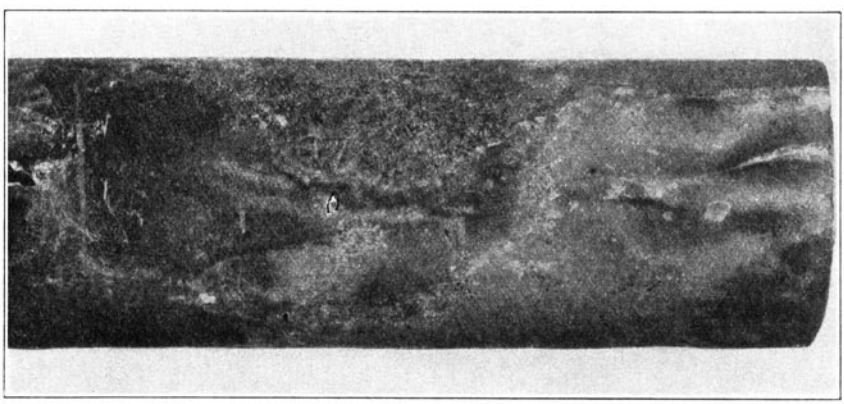


FIG. 4. SECTION OF ECONOMIZER TUBE SHOWING MECHANICAL ACTION, OR EROSION BY STEAM JET

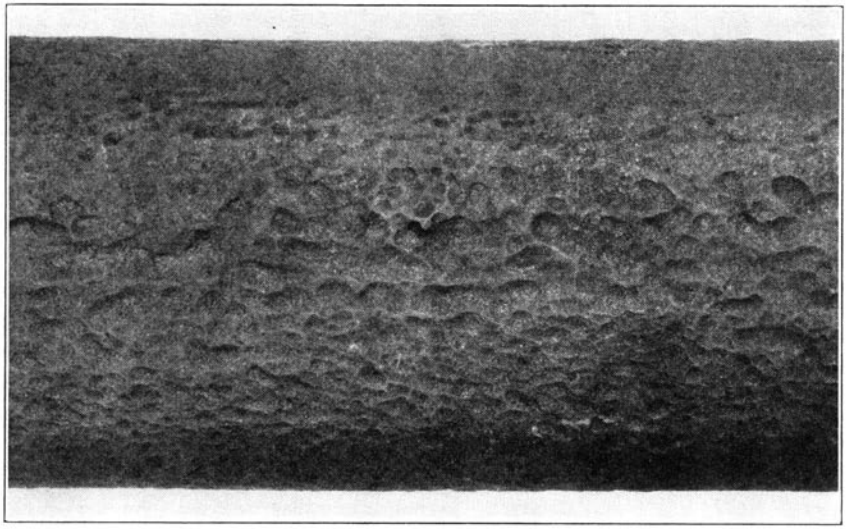


FIG. 5. CORRODED LEAD-COATED ECONOMIZER TUBE

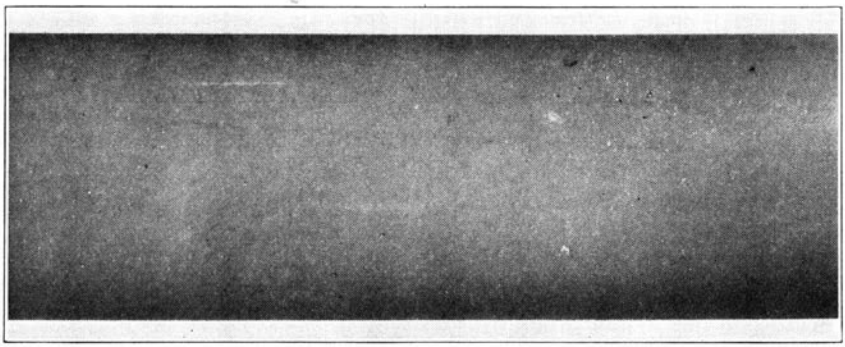


FIG. 6. SURFACE OF ENAMELED ECONOMIZER TUBE AFTER TWO YEARS OF SERVICE

(8) Differences in the types of construction of economizers and preheaters have shown no great differences in the rate of general corrosion. In some cases certain designs, however, cannot be used because of other difficulties arising from burning high-ash coal.

(9) Protective metallic coatings on the tubes have not withstood the attack. Figure 5 shows an example of a badly corroded lead coated tube. Enameled tubes will withstand the corrosion if mechanical difficulties involved in their use can be eliminated (Fig. 6).

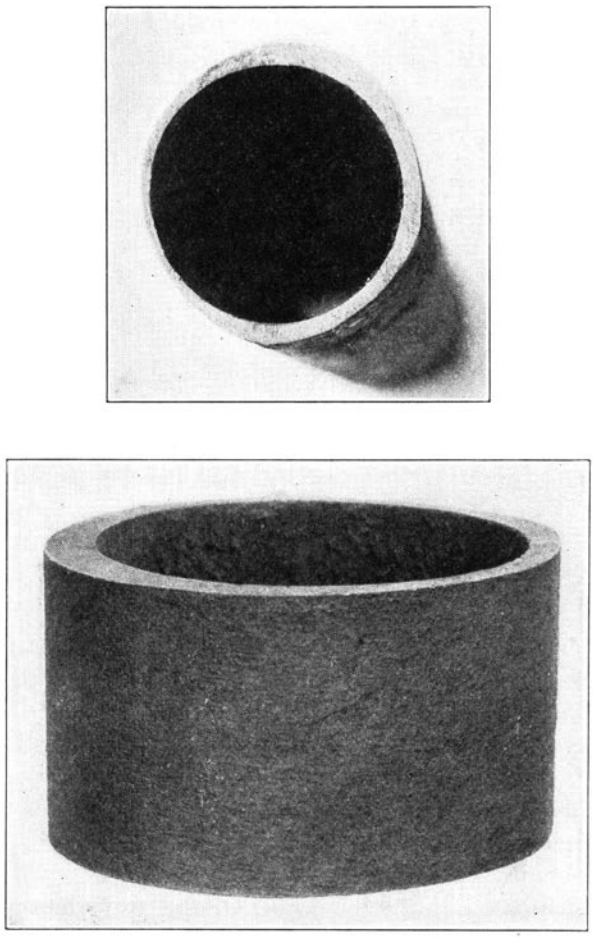


FIG. 7. GENERAL CORROSION OF ECONOMIZER TUBE

(10) The corrosion which has been found resulting from the combustion gases in waste heat boilers in gas plants is of a different nature and is less severe than that resulting from the burning of certain types of coal.

Other facts brought out by a closer study of the conditions will be presented in succeeding sections of this bulletin.

6. *Corrosion Caused by Leaks.* — It soon became apparent in making the survey of the power plants that two different types of corrosion are present as a result of conditions in the flue gases. First,

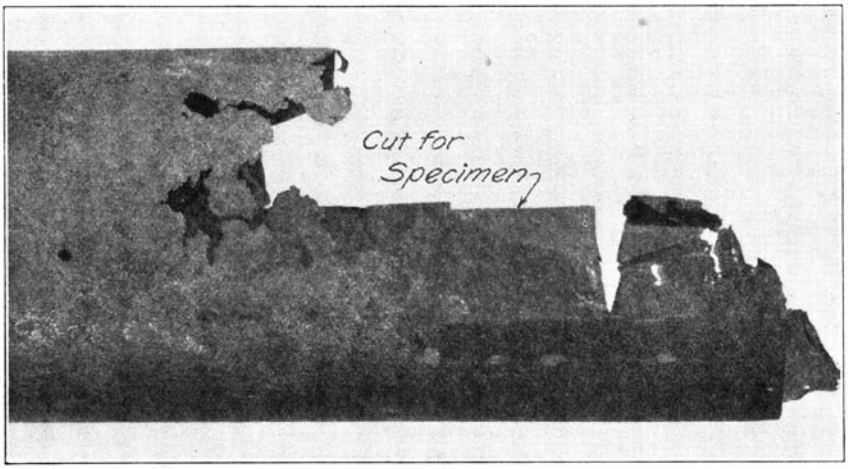


FIG. 8. SECTION OF CORRODED PREHEATER TUBE AFTER TWO YEARS OF SERVICE

there is a localized type of corrosion which is confined mostly to the ends of the economizer tubes and, second, there is a general corrosion which covers the entire tube surface in the colder part of the economizer, and in the preheater. Figure 7 shows the severity of this attack in the economizer, and Fig. 8 that on the preheater. While the chemical reactions which control the rate of these two forms of deterioration are exactly the same, it will be seen that the origins of the conditions are entirely different.

The local corrosion is caused by a high moisture content of the gas in the immediate vicinity of a leak. Of the two, this type of corrosion has proved the more severe. In fact, its results were almost disastrous to the use of economizers on high pressure boilers. The failure of the rolled-type of economizer construction to withstand the high pressures maintained in many plants cannot be entirely explained. The developments of leaks through the rolled joint may be due to the expansion and contraction of the tubes with temperature changes, or to some chemical action. In many cases the water escaping under high pressure cuts channels like worm holes along the surface of the joint. The development of such a leak is neatly illustrated in Fig. 9. Evidently, therefore, a joint made absolutely water-tight at the beginning will stand less chance of developing a leak after it has been in service than one which originally showed seepage. A trace of water in the joint itself will be sufficient to cause a slight corrosion. This

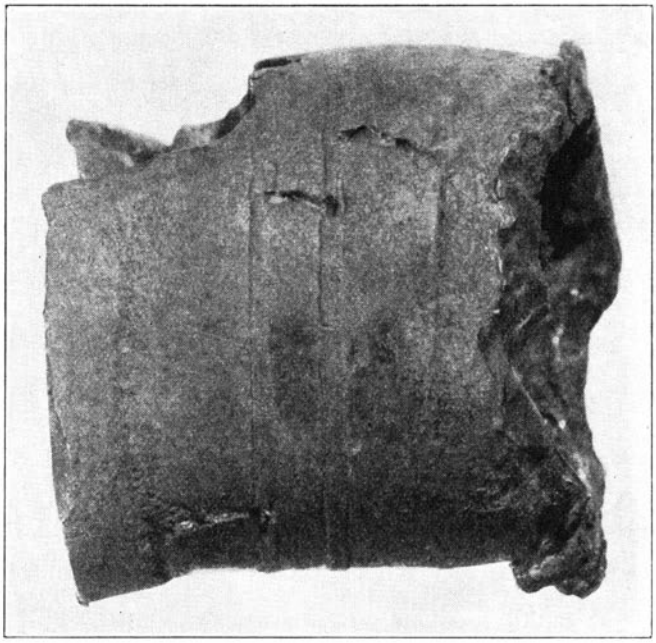


FIG. 9. DEVELOPMENT OF LEAK IN ROLLED JOINT

will decrease the resistance to the passage of water. Very soon a small jet of water will escape, and the high pressure will soon erode the opening until it is sufficient for a large leak. Unfortunately, a leak will not only damage the tube from which it originates, but will affect all those in its immediate vicinity. A part of the damage is caused by erosion by the direct water-steam jet, and a part by the corrosion resulting from the excess moisture. The latter is particularly bad in the presence of a scale deposited from the flue dust. While the character of this scale depends somewhat on the type of coal burned and on the methods of operation so that the local corrosion has been more severe in some plants than in others, very few plants have escaped the loss of some tubes due to the corrosion originating from leaks. New designs in economizer construction within the last few years fortunately make it possible to place all joints where leaks might occur entirely outside of the gas passage. While the leaks themselves have not been eliminated entirely, the conditions set up by them have been removed and the local corrosion has disappeared in those plants using this type of construction.

TABLE 4
CORROSION LOSSES IN POWER PLANT A RESULTING FROM LEAKS AROUND TUBE ENDS

Boiler Number	Days in Service	Days out of Service*	Tubes Replaced in Economizers
1	...	...	111
2	639	281	211
3	659	262	169
4	671	236	139
5	646	258	224
6	454	202	321
7	562	313	320
8	500	272	263
9	554	246	229
10	744	293	368
11	247	405	32
12	687	266	34
13	699	173	157
14	664	139	41
15	636	123	34

*Most of the outage was necessary for repairs in the economizer.

The general corrosion still exists, however, and is particularly severe in the preheaters of many plants (Fig. 8). It is true that even this form of corrosion has been decreased to some extent by the elimination of the source of part of the moisture content of the gases. While the work described in this bulletin was carried on mainly with the elimination of this type of corrosion in mind, it is believed that the same principles and results will apply to both types.

7. *Extent of Corrosion.*—The extent of the corrosion by flue gases varies greatly from plant to plant, depending not only upon the type of fuel used but also upon the conditions of operation. A brief summary of the severity of the corrosion in the plants investigated follows:

In plant A the loss of tubes during the first two years of operation was extremely large. Most of the loss could be traced to the prevalence of a large number of leaks around the tube ends. The high pressures used in this plant tended to increase the cutting action of jets of steam. After this condition of leakage was removed by the use of the new type of return-bend economizer tubes, most of the tube loss was eliminated. There remains, however, a general corrosion over the entire lower portion of the economizer and in the preheater which necessitates the replacement of economizer tubes after two to three years of service, and of approximately half the tubes in each preheater after two years of service. The tube loss in this plant during the time the rolled type of tubes was in use is shown for 15 boilers in Table 4. The average penetration due to the

TABLE 5
AVERAGE PENETRATION DUE TO GENERAL CORROSION* OF ECONOMIZER TUBES IN POWER PLANT A

Boiler	Days in Service	No. of Tubes	Penetration,‡ in.					
			0	0-1/64	1/64-1/32	1/32-3/64	3/64-1/16	>1/16
Top Row (gas entrance)								
1†	293	25	14	9	2	0	0	0
2	231	25	14	10	1	0	0	0
3	382	25	7	4	4	2	3	5
4	289	25	5	17	3	0	0	0
5	354	22	5	10	3	1	2	1
6	503	25	8	7	7	2	1	0
Bottom Row (gas exit)								
1	293	5	0	1	4	0	0	0
2	231	7	0	1	6	0	0	0
3	382	6	1	1	0	0	2	2
4	289	8	4	4	0	0	0	0
5	354	..	..	..	..	..	..	..
6	503	8	0	2	0	1	0	5

*The tubes were all new and there were no water leaks in the gas passage.
†Numbers do not refer to any particular boiler.
‡Penetration equals one-half the loss in diameter.

TABLE 6
CORROSION COST DATA—PLANT C

Economizer Maintenance Costs

First year.....$456.00 per economizer
Second year.....$1392.00 per economizer
Estimated cost of economizer maintenance alone (regular maintenance) per year—$25.00.

Air Preheater Maintenance Cost

First year.....$73.00 per preheater
Second year.....$1492.00 per preheater
Estimated cost of air preheater maintenance alone (regular maintenance) per year—$10.00

general corrosion, which was determined by calipering the top and bottom rows of tubes in 6 economizers, is shown in Table 5.

The corrosion in plant B was similar in degree and in cause to that described for plant A.

Corrosion in plant C includes both the localized type due to leakage and the general corrosion. The first indications of deterioration in the economizer were noticed after about 10 months. After this

time tube renewals were frequent. In 19 months of operation 1600 tube replacements had been made. After 26 months the entire economizers were rebuilt with return-bend tubes so that the leaks in the gas passage were eliminated. The new tubes were of copper-molybdenum steel and were of three thicknesses, ¼ in., 5/16 in., and ⅜ in., the heavy tubes being placed in the most active corrosion section. The general corrosion with the accompanying loss of tubes has not ceased. Table 6 shows the actual cost of economizer and preheater maintenance for the first two years of operation as compared with the estimated cost.

Corrosion in the air preheaters at this plant is also severe. These are of the plate type construction. A complete set of new elements was required after 26 months of service. The corrosion in the preheater takes place at the hot end, where the gases enter, and extends for a distance of about 4 ft. The corrosion follows to some extent the path of the air, but is all on the gas side. It has been the practice of the plant to wash the preheaters and economizers with water about every three weeks. This is done when the boilers are cold.

A noticeable feature of the corrosion at plant C is the location and the nature of the attack. In the ordinary boilers the severe corrosion definitely starts at a point about 20 rows of tubes from the bottom (gas exit) of the economizer and extends into the preheater (see Fig. 10a). The temperature of the metal at which the corrosion begins has been determined to be about 260 deg. F. In the reheat boilers due to higher gas temperatures the corrosion is shifted downward about 5 rows of tubes. The nature of the corrosion in the economizer tubes is shown in Fig. 10b. The attack is most severe at four points on the periphery of the tube. These have been shown to correspond to points immediately above and below the horizontal diameter, and to be those on which the deposit from the flue dust is thickest,—the pattern being obtained by the arrangement of the tubes in a staggered fashion.

In plant D an integral type of economizer installed in the same manner as the boiler proper is used. The leakage in the economizer amounts to about 95 per cent of the leakage of the whole system. Around each leak there is a zone of corrosion and many tubes are lost from this condition. After five years of operation all economizers have been replaced by the same design with precautions taken to eliminate the contraction and expansion of the metal with changes in temperature in the zone where leakage might be serious.

In plant E most of the corrosion has been located in the colder parts of the preheater. This has necessitated the replacement of

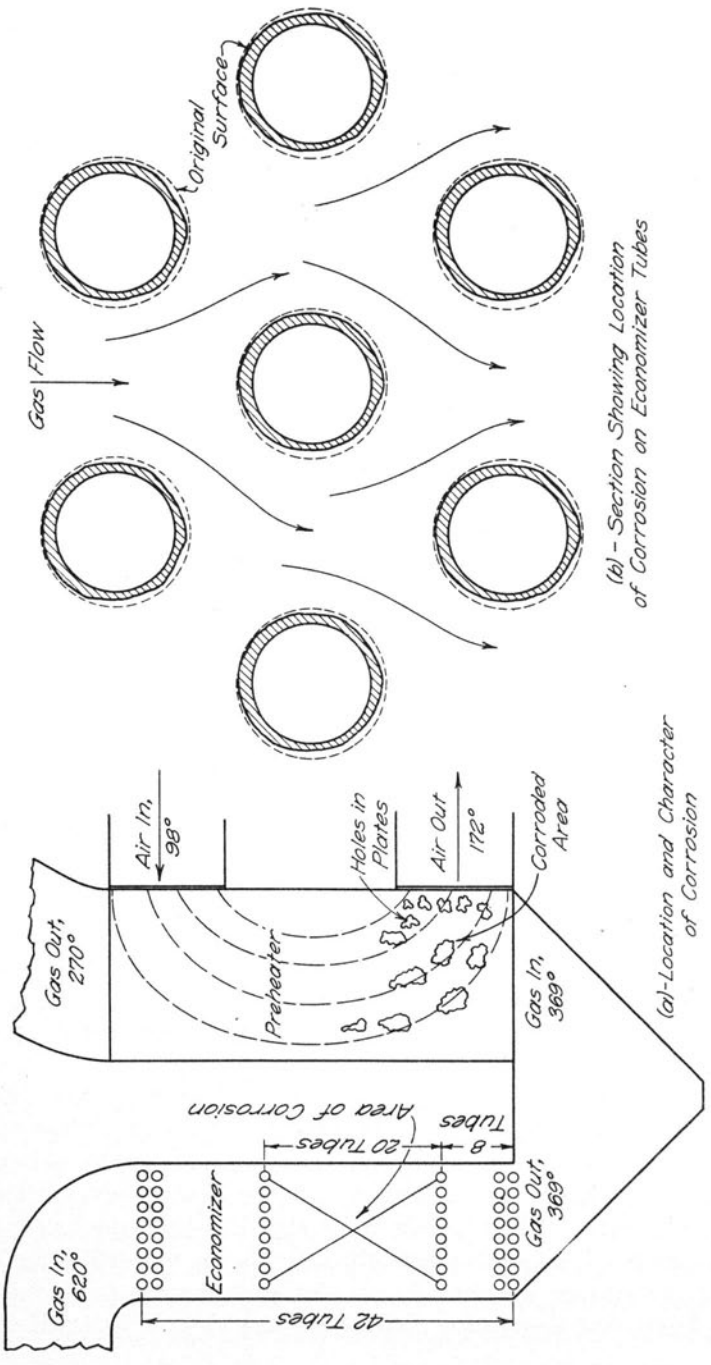


FIG. 10. DIAGRAMMATIC SKETCH SHOWING LOCATION AND CHARACTER OF CORROSION AT PLANT C

several preheater units after three years of operation. The loss in economizer tubes is negligible.

In plant F the low operating pressure permits the use of cast-iron economizer tubes. The loss of tubes here has been steadily increasing since the second year of operation. In the tenth year of operation 295 tubes, or approximately 3 per cent of the total, were replaced in thirty-one boilers.

In plant G two types of economizers have been in service, viz., an external economizer with cast-iron fins and an integral bare-tube economizer. No corrosion has developed in the former. Approximately 15 tubes have been replaced in the latter. The point of attack near the ends of the tubes indicates that the loss was due to localized corrosion caused by leaks.

In plant H the corrosion is slight, and has been due to localized leaks. Only 5 tubes have been replaced in the plant in three years of operation. The general corrosion over the entire tube surface during this time has penetrated about $\frac{1}{128}$ in.

The corrosion in plant I presents an especially interesting case. The boilers were designed to operate on the residues from a petroleum refinery. The fuel varies considerably, including natural gas, pulverized petroleum coke, acid lubricating sludge, acid tar, fuel oil, soda bottoms, neutral sludge, wax tailings, and certain combinations of these. The lubricating sludge at times contains as much as 25 per cent sulphuric acid. The sulphur content of the other petroleum products varies from approximately 0.7 per cent for the coke to 3 per cent in the acid tar. A complete description of the qualities of the flue gases for each fuel is given in Table 10. Although this plant had been in operation for only a few months when visited, considerable corrosion had taken place in the preheaters. Many perforations could be found in front of the cold-air intake. The general corrosion extended throughout the preheater and into the economizer. The attack in the hotter zones was, of course, less than that at the lower metal temperatures.

In plant J, where the same fuel as that at plant B is used, differing only in that it is burned in the pulverized form, only 3 tubes have been replaced in the economizer, in spite of the use of the old type of rolled joint construction. There is a large temperature variation in the economizer here brought about by shutting down the boiler entirely at night. The general corrosion, as shown by calipering the tubes, has penetrated less than $\frac{1}{32}$ in. during two years of operation.

Loss due to corrosion in the plants designated by the letters K to O

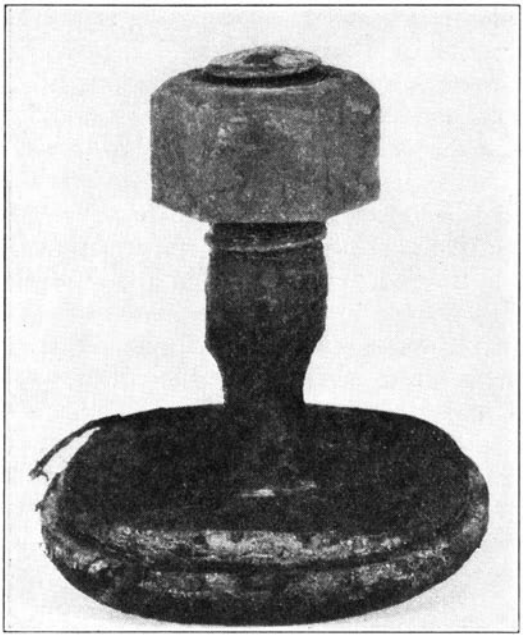


FIG. 11. CORRODED HAND-HOLE PLATE

has been limited to that caused by the localized type. Practically every plant has reported some corrosion caused by leaks. Figure 11 shows an interesting case of corrosion of a hand-hole bolt on an economizer in plant K. Moisture from a leaky gasket has caused the ash from pulverized fuel to attack the metal in spite of the fact that a low sulphur coal is used.

B. Sulphur Compounds in Flue Gases

8. *Reactions during Combustion.*—The burning of coal in a furnace involves many different chemical reactions. Of these, the ones taking place in the combustion of carbon and hydrogen have been fairly well determined in previous investigations. Without going into the exact mechanism of the reactions, the ultimate result is the production of water vapor and of the oxides of carbon in the gaseous form. The chemical reactions in which the impurities in the coal enter, however, are not quite so simple. These substances are not distributed uniformly throughout the coal and are of quite variable composition. Some of them may pass into the ash pit unchanged, while others may be carried away by the gases, and still others undergo various degrees

of oxidation, some fusing and some remaining solid. The general result is the formation of a mixture of solid compounds composed of various silicates and aluminates and containing small percentages of calcium, sodium, magnesium, and iron.

The results of the combustion of the sulphur in coal are not definitely known. It has been assumed, however, that for the most part it is first oxidized to sulphur dioxide in the furnace and later, in the colder portions of the system, this gas is further oxidized at least partially to sulphur trioxide. In a survey of the conditions at various power plants, the Bureau of Mines* has obtained some data which apparently justify these conclusions. The method of obtaining these results, however, is subject to some questioning. For this reason, and because of the importance of sulphur compounds in the corrosion process, as shown by the survey of the plants, it seemed desirable to determine accurately the concentration of sulphur dioxide and sulphur trioxide in the furnace gases. To this end some little time and attention was devoted to the perfection of a method that would produce more accurate results than those formerly obtained.

9. *Determination of Sulphur Dioxide and Sulphur Trioxide in Flue Gases.*—A method was developed which, in the laboratory, gave good results for the determination of both sulphur dioxide and sulphur trioxide in the gases. Because of inherent difficulties in the method, however, such as the clogging of the filters with fine dust and the need of a strong pump to draw the gases, it was later discarded in favor of one which proved more rapid and easier to carry out. A complete description of both methods, and a comparison with the results obtained by the methods previously suggested, is given in Appendix A.

The first method was used at plants A, C, H, and J. The second method was used at plant I. The results obtained by the two methods are entirely comparable, and form an important contribution to the study of the causes of the corrosion, and of the reactions which the sulphur compounds undergo in a boiler furnace.

In the analyses, efforts were made in all cases to secure a representative sample of gas at the various points. To this end at least three samples were taken at each point over a period of two hours and at various boiler ratings. An exploration of the gas stream was made by drawing samples from points at various distances from the side wall. A correction for the amount of excess air present was made

*Sherman and Rice, "Refractories Service Conditions," Mech. Eng., vol. 48, pp. 1115, 1389, 1926; cf. also, Barclay, "The Sulphur Problem in Burning Coal"; Bureau of Mines Tech. Paper No. 435, 1928.

by determining the sulphur-carbon ratio in the gas. This precaution has been suggested by Sherman and Rice.* In order to do this the carbon dioxide and oxygen content of the gases were determined simultaneously with the sulphur analyses. The samples for these analyses were drawn, of course, from the same point. The sulphur-carbon ratio was then determined by the formula

$$\frac{S}{C} = \frac{2.667\ (\text{per cent } SO_2 + \text{per cent } SO_3)}{\text{per cent } CO_2}$$

These values should entirely eliminate the errors due to any variation in excess air, and for the most part those due to stratification. The values for any two points in the boiler and for any two plants are directly comparable. From them the fraction of sulphur in the coal passing into the gases may be obtained by

$$\frac{\text{Ratio S/C in gas}}{\text{Ratio S/C in coal}} = \text{fraction of S in gas.}\dagger$$

In the same way the extent of the oxidation of the sulphur was determined by calculating the ratio of SO_3/SO_2 in the gas. A high value of this ratio indicates considerable oxidation of the SO_2 to SO_3. The same relation is also expressed as per cent sulphur existing as SO_3. In this case

$$\text{per cent S as } SO_3 = \frac{(SO_3/SO_2)100}{1 + (SO_3/SO_2)}$$

The results of the analyses for the five plants, A, C, H, I, and J, are shown in Tables 7 to 11. Each of the values given represents an average of all the analyses performed for any one point in the gases. In most cases three samples were drawn from each point. The approximate constancy of the sulphur-carbon ratio indicates that most of the errors of analysis were eliminated. Changes in the character of the coal, of course, would account for some variation. While the fluctuations of the SO_3/SO_2 ratio are somewhat larger than those of the other ratio, the actual values are all extremely low.

*Sherman and Rice, Mech. Eng., vol. 49, p. 1085, 1927.

†This value is correct only when the percentage of carbon remaining in the ash is negligible. The exact value of "fraction of S in gas" is given by multiplying the ratio given above by $\left(1 - \frac{R-A}{C}\right)$ where A, C, and R, respectively, represent the ash, carbon, and refuse, expressed as percentages of the dry fuel.

TABLE 7
COMPOSITION OF FLUE GASES AT PLANT A

Boiler No.	Point of Sampling	Distance from Front of Boiler, ft.	Distance from Side of Boiler, ft.	No. of Samples	SO_2		SO_3		O_2	CO_2	Ratio S/C wt.	Ratio SO_3/SO_2 vol.	Per cent S as SO_3
					Vol. per cent	Grains cu. ft.	Vol. per cent	Grains cu. ft.	Vol. per cent	Vol. per cent			
1	1st pass of boiler	4	5	2	0.289	3.61	0.0060	0.094	8.6	10.8	0.073	0.020	2.0
1	1st pass of boiler	4	10	2	0.313	3.91	0.0086	0.134	7.8	11.6	0.074	0.028	2.7
1	1st pass of boiler	6	10	2	0.300	3.74	0.0122	0.190	8.0	11.5	0.072	0.041	3.9
2	1st pass of boiler	2	5	2	0.295	3.68	0.0060	0.094	...	12.6	0.064	0.020	2.0
2	1st pass of boiler	2	10	3	0.347	4.33	0.0018	0.028	...	14.2	0.067	0.034	3.3
2	1st pass of boiler	4	5	3	0.384	4.79	0.0030	0.047	...	13.1	0.079	0.008	0.8
2	1st pass of boiler	4	10	3	0.373	4.66	0.0143	0.223	4.1	15.0	0.069	0.039	3.8
2	1st pass of boiler	6	5	4	0.279	3.48	0.0123	0.192	...	12.1	0.064	0.041	3.9
2	1st pass of boiler	6	10	2	0.328	4.09	0.0148	0.231	...	12.8	0.071	0.045	4.3
2	2nd pass of boiler	10	5	3	0.268	3.34	0.0154	0.240	...	9.6	0.078	0.058	5.5
2	2nd pass of boiler	10	10	3	0.346	4.32	0.0126	0.196	...	13.0	0.074	0.037	3.6
2	Economizer outlet	2	5	3	0.270	3.37	0.0050	0.078	9.0	10.9	0.068	0.018	1.8
2	Economizer outlet	2	10	2	0.274	3.42	0.0050	0.078	9.5	10.0	0.075	0.018	1.8
2	Induced fan inlet	..	2	6	0.100	1.25	0.0019	0.030	15.6	4.4	0.063	0.019	1.9
3	1st pass of boiler	4	5	2	0.156	1.94	0.0016	0.025	....	5.4	0.078	0.012	1.2
3	1st pass of boiler	4	10	3	0.197	2.46	0.0059	0.092	10.8	8.0	0.075	0.028	2.7
3	1st pass of boiler	6	5	2	0.207	2.58	0.0035	0.055	11.8	7.8	0.073	0.016	1.6
3	1st pass of boiler	6	10	3	0.319	3.98	0.0086	0.134	7.5	11.5	0.074	0.027	2.6
3	2nd pass of boiler	10	5	3	0.268	3.34	0.0035	0.055	9.3	10.1	0.072	0.014	1.4
3	2nd pass of boiler	10	10	3	0.274	3.42	0.0152	0.237	9.0	10.6	0.073	0.056	5.3
3	Economizer outlet	2*	5	3	0.240	2.99	0.0071	0.111	11.4	8.6	0.073	0.030	2.9
3	Economizer outlet	2*	10	3	0.272	3.39	0.0068	0.106	9.7	10.2	0.073	0.025	2.4
3	Economizer outlet	2*	15	3	0.317	3.96	0.0079	0.123	8.0	11.7	0.074	0.025	2.4
	Average				0.279	3.48	0.0082	0.128	...	10.7	0.072	0.029	2.8

*From top of duct between economizer and preheater.

TABLE 8
COMPOSITION OF FLUE GASES AT PLANT C

Point of Sampling	No. Samples	SO_2		SO_3		CO_2 Vol. per cent	O_2 Vol. per cent	Ratio S/C wt.	Ratio SO_3/SO_2 vol.	Per cent S as SO_3
		Vol. per cent	Grains per cu. ft.	Vol. per cent	Grains per cu. ft.					
Economizer inlet....	6	0.108	1.35	0.0032	0.050	11.4	7.8	0.026	0.031	3.0
Economizer outlet...	6	0.0914	1.14	0.0025	0.039	....	...	0.022	0.028	2.7
Average.....		0.100	1.25	0.0028	0.044	11.4	7.8	0.024	0.030	2.9

TABLE 9
COMPOSITION OF FLUE GASES AT PLANT H

Point of Sampling	Distance from Front ft.	Distance from Side ft.	No. of Samples	SO_2		SO_3		CO_2 Vol. per cent	O_2 Vol. per cent	Ratio S/C wt.	Ratio SO_3/SO_2 vol.	Per cent S as SO_3
				Vol. per cent	Grains per cu. ft.	Vol. per cent	Grains per cu. ft.					
In superheater loop...	3	5	3	0.117	1.46	0.0049	0.076	13.3	6.0	0.0233	0.043	4.1
In superheater loop...	3	10	6	0.131	1.63	0.0006	0.009	14.5	4.9	0.0281	0.005	0.5
In 2nd pass of boiler...	12	5	4	0.194	2.42	0.0005	0.008	14.2	5.0	0.0365	0.003	0.3
In 2nd pass of boiler...	12	10	3	0.148	1.85	0.0004	0.006	13.6	6.0	0.0290	0.003	0.3
Economizer outlet....	2*	4	2	0.038	0.47	0.0009	0.014	5.8	14.8	0.0180	0.023	2.2
Economizer outlet....	2*	8	6	0.098	1.22	0.0019	0.030	13.4	5.7	0.0196	0.019	1.9
Average.....				0.121	1.51	0.0015	0.023	12.5	7.1	0.0258	0.016	1.6

*From top of passage between economizer and preheater.

TABLE 10

COMPOSITION AND DEW-POINT OF FLUE GASES AT PLANT I

All samples drawn from between economizer and preheater, 4 ft. from side wall

Fuel	Dew-point deg. F.	SO_2		SO_3		CO_2 Vol. per cent	Ratio S/C wt.	Ratio SO_3/SO_2 vol.	Per cent S as SO_3
		Vol. per cent	Grains per cu. ft.	Vol. per cent	Grains per cu. ft.				
Acid sludge, 4 burners, Nat. gas	138	0.112	1.40	0.0266	0.415	....	.....	0.237	19.1
Acid sludge, 10 burners, Nat. gas	132	0.103	1.28	0.0179	0.279	9.3	0.035	0.174	14.7
Acid sludge, 10 burners, Nat. gas	131	0.141	1.76	0.0207	0.323	11.8	0.036	0.147	12.8
Acid sludge, 10 burners, Nat. gas	131	0.150	1.88	0.0157	0.245	11.5	0.038	0.105	9.5
Soda bottoms, 2 burners, Nat. gas	144	0.057	0.92	0.0151	0.235	11.0	0.017	0.265	21.0
Soda bottoms, 2 burners, Nat. gas	144	0.039	0.49	0.0097	0.151	9.6	0.014	0.249	19.8
Soda bottoms, 5 burners, Nat. gas	148	0.000	0.00	0.0037	0.058	10.4	0.001	.....	....
Soda bottoms, 5 burners, Nat. gas	148	0.006	0.075	0.0009	0.014	10.9	0.002	0.150	13.0
Soda bottoms, 4 burners, Nat. gas									
Acid tar, 4 burners, Nat. gas	151	0.031	0.384	0.0018	0.028	9.6	0.009	0.058	5.4
Acid tar, 8 burners, Nat. gas	...	0.162	2.027	0.0114	0.178	11.6	0.040	0.070	6.6
Acid tar, 8 burners, Nat. gas	...	0.163	2.039	0.0083	0.130	11.1	0.041	0.051	4.8
Acid tar, 8 burners, Nat. gas	147	0.151	1.884	0.0107	0.167	10.9	0.040	0.070	6.7
Acid sludge, 6 burners, Nat. gas	132	0.163	2.035	0.0276	0.431	10.0	0.051	0.169	14.5
Acid sludge, 6 burners, Nat. gas	132	0.157	1.959	0.0364	0.568	10.2	0.050	0.232	18.8
Acid sludge, 6 burners, Nat. gas	132	0.150	1.872	0.0304	0.474	10.0	0.048	0.203	16.8
Acid sludge, 6 burners, Nat. gas	133	0.186	2.315	0.0164	0.253	10.4	0.052	0.088	8.1
Natural gas alone	142	0.014	0.174	0.0003	0.005	9.4	0.004	0.021	2.1
Natural gas alone	142	0.010	0.125	0.0002	0.003	9.4	0.003	0.020	2.0
Natural gas alone	138	0.009	0.112	0.0003	0.005	9.2	0.003	0.033	3.2
Fuel oil alone	115	0.100	1.248	0.0097	0.151	10.5	0.028	0.097	8.8
Fuel oil alone	115	0.110	1.372	0.0154	0.240	11.8	0.028	0.140	12.3
Fuel oil alone	116	0.116	1.448	0.0138	0.215	12.3	0.028	0.119	10.6
Average	135	0.097	1.210	0.0133	0.209	10.5	0.028	0.137	12.1

TABLE 11
COMPOSITION OF FLUE GASES AT PLANT J—PULVERIZED FUEL BOILER

Point of Sampling	Distance from Front, ft.	Distance from Side, ft.	No. of Samples	SO_2		SO_3		O_2 Vol. per cent	CO_2 Vol. per cent	Ratio S/C wt.	Ratio SO_3/SO_2 vol.	Per cent S as SO_3
				Vol. per cent	Grains per cu. ft.	Vol. per cent	Grains per cu. ft.					
1st pass of boiler.....	4	5	3	0.414	5.17	0.0046	0.072	5.0	14.3	0.078	0.011	1.1
1st pass of boiler.....	4	10	3	0.387	4.83	0.0027	0.042	4.0	15.3	0.068	0.007	0.7
1st pass of boiler.....	8	5	3	0.421	5.25	0.0032	0.050	5.9	13.3	0.085	0.008	0.8
1st pass of boiler.....	8	10	3	0.453	5.65	0.0034	0.053	3.6	15.6	0.078	0.007	0.7
Economizer outlet....	..	5	2	0.479	5.98	0.0036	0.056	5.0	14.2	0.090	0.008	0.8
Economizer outlet....	..	10	2	0.416	5.19	0.0032	0.050	6.3	12.9	0.086	0.006	0.6
Economizer outlet....	..	5	3	0.347	4.33	0.0020	0.031	8.2	11.1	0.085	0.006	0.6
Induced fan inlet.....	..	4	4	0.385	4.80	0.0028	0.044	7.6	11.8	0.087	0.007	0.7
Average.....				0.413	5.15	0.0032	0.050	5.7	13.6	0.082	0.008	0.8

10. *Summary.*—The most significant facts indicated by the data on the gas composition are:

(1) The SO_3 values are extremely low at all plants.

(2) The SO_3 concentrations in the gases from the pulverized fired coal are 70 per cent less than those from the same coal stoker fired.

(3) There is no tendency for the SO_3 concentration to increase as the temperature decreases.

(4) The SO_3/SO_2 ratio is independent of the oxygen concentration in the gases.

(5) The S/C ratios indicate that about 70 per cent of the sulphur of the coal enters the gas when the coal is fired on a stoker, and that this is increased to about 90 per cent when the coal is fired in the pulverized form.

(6) When petroleum residues containing large quantities of sulphuric acid are burned in a boiler furnace approximately 85 per cent of the sulphur is converted to SO_2. The SO_3 concentrations in these gases are but slightly higher than the corresponding values in the gases from high sulphur coal. (The higher values may be accounted for partially by errors that cause low results in the first method used for analysis. See Appendix A for discussion.)

(7) Taking all results into consideration, the oxidation of SO_2 to SO_3 in flue gases is very small.

All of these facts bear an important relation to the combustion of the forms of sulphur in the coal. A more complete discussion of them will be given after other data on the character of the flue gases are presented.

C. Dew-Point of Flue Gases

11. *Importance of Dew-Point in Corrosion by Flue Gases.*—In the corrosion of metals by gases there is evidently a change in the type of reactions that may take place when the temperature is lowered to a point where a liquid phase may be formed on the surface of the metal. Above this temperature the corrosion, like all other reactions between gases and solids, would be slow. The formation of such a liquid phase would influence the rate of corrosion not only because of the presence of a film of acid, but also because other corroding agents will be brought into solution, and thus into closer contact with the metal, with a consequent better opportunity for reacting. In all probability the rate of corrosion would be greatest at the temperature of the dew-point because of the combined action of the acid film and of substances brought into solution. At higher temperatures there is the possibility of some reaction between the gas and the metal, but

this would be extremely small. At temperatures below the dew-point the rate of corrosion probably decreases due to the usual temperature coefficient of the chemical reactions.

12. *Previous Estimates of Dew-Point of Flue Gases.*—Various estimates of the dew-point of flue gases have been made. Unfortunately, most writers have not realized that a trace of sulphuric acid vapor materially affects the temperature at which a liquid will first form. Although the usual definition for the dew-point is "the temperature at which a given mixture of air and water vapor is saturated with water vapor,"* this idea is too specific and should be enlarged to include gases that contain two or more condensable vapors. In such a case the dew-point may better be defined as *the highest temperature at which a liquid may exist in equilibrium with the gas.* This temperature will then depend upon the concentration of each condensable vapor in the gas and upon the characteristics of these substances. On account of the high boiling point (i.e., the extremely low vapor pressure) of sulphuric acid, a trace of this vapor in the gas phase is sufficient to cause a very high dew-point.

Estimates of the dew-point of flue gases based on the percentage of water vapor in the gases have for the most part shown that a liquid will first appear between 90 and 120 deg. F. It may be shown by calculation, based on the partial pressures of sulphuric acid and water over acids of high concentrations, that this temperature is 20 to 100 deg. F. too low, depending upon the concentration of sulphuric acid vapor in the gas.

13. *Electrical Method for Determination of Dew-Point.*—Because of the importance of the dew-point in the corrosion by flue gases, an attempt to determine the value by some direct method seemed worth while. The results could also be used as a check on the concentration of sulphur trioxide in the gases as obtained by the analytical method outlined. Of the methods that have been proposed for the determination of the dew-point, the ordinary psychrometric procedure, based on the difference in temperatures of a wet and a dry bulb, of course, would be inapplicable to flue gases, because the principle of the method assumes that water vapor is the only condensable substance in the gas. In order to be able to use such a method not only would the composition of the liquid and of the gas phase be required, but also a large amount of data on the heats of vaporization of the solutions formed. Other methods that have been described in the litera-

*Walker, Lewis, and McAdams, "Principles of Chemical Engineering," ed. 2, p. 442, McGraw-Hill Book Co., New York, 1927.

ture for the direct determination of the dew-point are those based on the observation of a highly polished metal surface, the temperature of which can be adjusted until the dew forms, and over which the gaseous mixture is passed. The difficulties in observing the formation of the liquid phase from flue gases are apparent. Furthermore, since the dew-point varies with the operation of the boiler, some method of recording is greatly desirable.

The method finally selected for determining the dew-point is based on the principle of electrical conductivity of a glass surface. A complete description has been published elsewhere.* Essentially the apparatus consists of a glass bulb, on the outer surface of which are imbedded two platinum electrodes. Adjacent to these electrodes, and also on the surface of the glass, is the junction of a thermocouple. The flue gases are drawn around the glass bulb by means of an aspirator. The temperature of the bulb is varied by means of a jet of cold air directed against the inside. When the temperature of the glass surface has been decreased until a liquid phase first forms, the conductivity of the gap between the two electrodes increases greatly. This increase in conductivity can be further amplified by means of the familiar thermionic valve. By the use of a suitable relay, the formation and disappearance of the liquid phase may be caused to make and break a heating circuit. Thus, by inserting a heating coil of resistance wire in the air stream directed against the back of the glass bulb, the formation of the dew will cause the temperature of the air to rise. The glass surface thereby increases in temperature and the dew evaporates. The cycle is then repeated. In the record of the temperature of the glass surface as determined by the thermocouple, the minimum points on the temperature curve correspond to the dew-point.

14. *Results of Dew-Point Determinations.*—Such an apparatus has been employed to determine the dew-point at the three power stations, A, H, and I. Figures 12 and 13 show typical variations of the dew-point for the first two plants. (The dew-point curves have been plotted from the minima of the recorder readings.) For comparison, the rate of evaporation during the same period of time has been plotted on the same charts. The values plotted were taken from Bailey Boiler Meter records. As might be expected, the dew-point fluctuations agree with those of the boiler rating. This is particularly noticeable in the case of plant A. Here a variation from 110 to 80 deg. C. (230 to 176 deg. F.) was caused by a drop in the evaporation of from

*"An Electrical Method for the Determination of the Dew-Point of Flue Gases," Univ. of Ill. Eng. Exp. Sta. Circular 20, 1929.

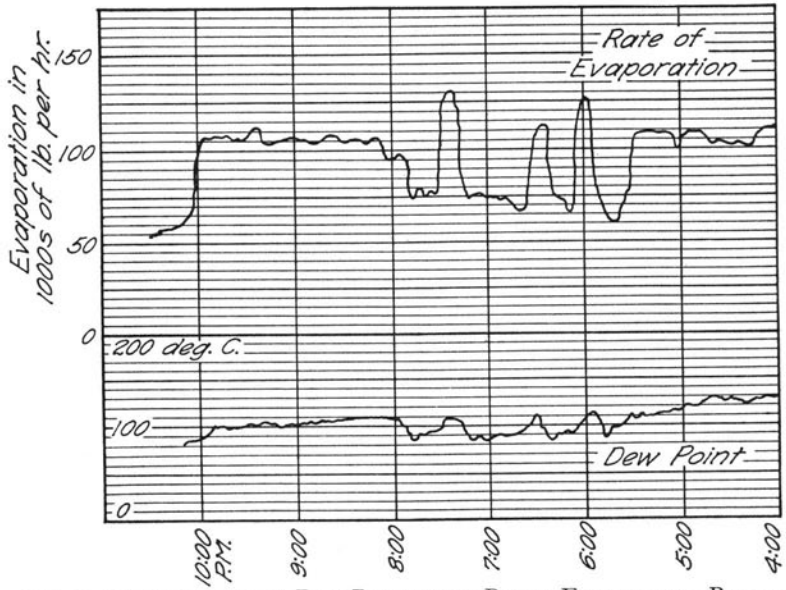


FIG. 12. FLUCTUATIONS IN DEW-POINT WITH BOILER EVAPORATION—PLANT A

110 000 to 60 000 lb. of steam per hour. The changes are undoubtedly due to a decrease in the concentrations of sulphur trioxide and water vapor in the gases, which are determined by the amount of coal fired and the excess air used. Fluctuations of the dew-point in the case of plant H are not so noticeable as those in plant A where a higher sulphur coal is used. The addition of moisture to the gases during the soot-blowing operation, however, causes a noticeable increase in the dew-point.

The values for dew-point as determined by this method for the gases from the various types of fuels burned at plant I are shown in Table 10. The condensation temperature varies slightly with the type of fuel burned, and is highest when a large portion of natural gas is burned with a fuel giving high SO_3. Natural gas, as a fuel, gives a relatively large amount of water vapor in the flue gases due to a large hydrogen content. The low dew-point in the case of fuel oil seems surprising. A confirmation of the values was found, however, in the absence of condensation on the glass sampling tube used for the sulphur determinations which were run simultaneously with the dew-point determinations. A heavy condensation was always noticed in drawing the samples when the other fuels were being burned.

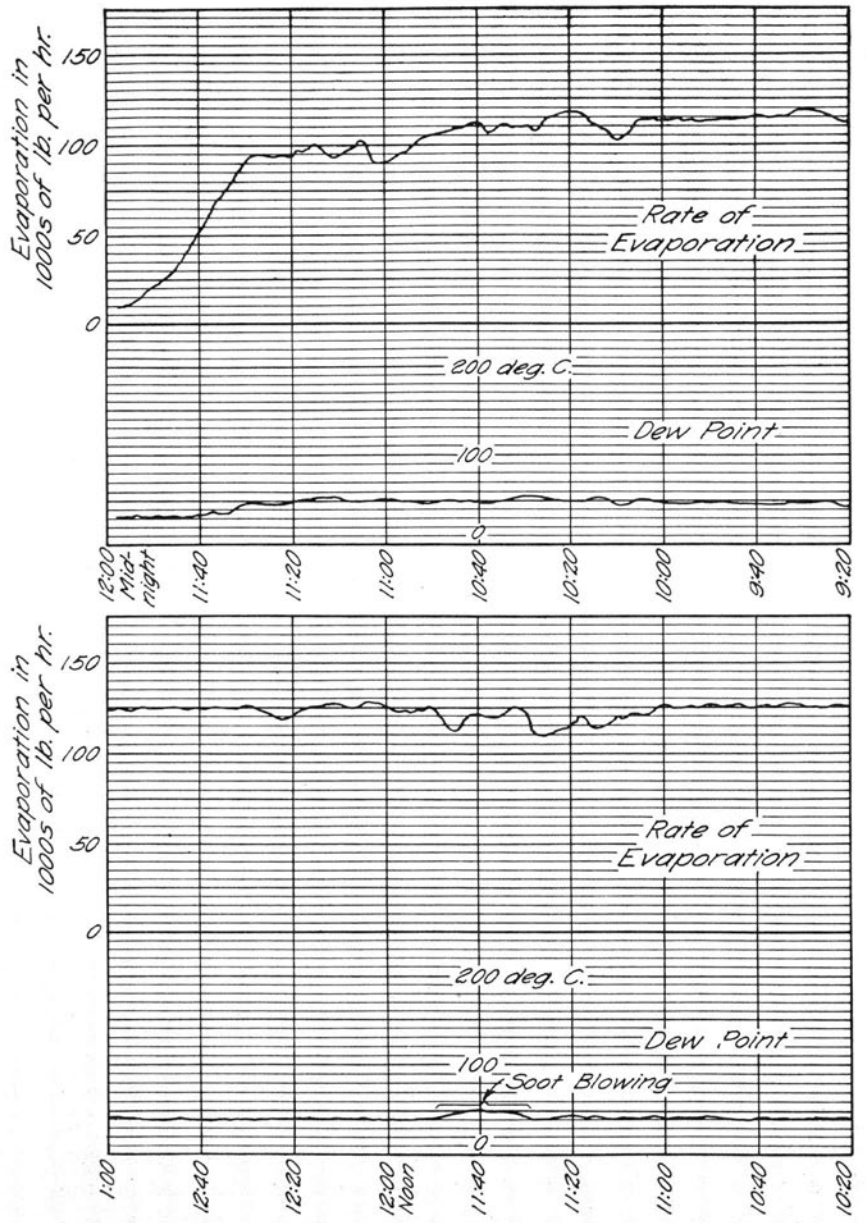


FIG. 13. FLUCTUATIONS IN DEW-POINT WITH BOILER EVAPORATION—PLANT H

Although the values obtained at plant I for the dew-point are somewhat lower than those found at plant A where the gases had approximately the same composition it is believed that the lower values are correct. The apparatus used at the latter plant was the first constructed for dew-point determination by this method, and it is possible that too great amplification was used. The accuracy of the method was later checked against the calculated dew-point of a gas containing water vapor in the absence of SO_3. The instrument showed the appearance of the liquid phase at 105.8 deg. F., whereas the calculated dew-point from an analysis of the gas was 106.0 deg. F. This agreement is perhaps fortuitous, and is probably better than that corresponding to the accuracy of the instrument, especially if sulphur trioxide is present. All other indications show that the determined values are within 5 deg. F. of the correct values. The data obtained at plants H and I were reproducible and constant except for fluctuations due to changes in fuel, boiler rating, or other operating conditions, such as soot-blowing, which manifestly would affect the dew-point of the gases.

15. *Summary: Effect of Sulphur Trioxide and Hygroscopic Substances on Temperature of Condensation.*—In view of the important relationship between the condensation temperature and corrosion the following facts should be emphasized:

(1) The dew-point of flue gases as determined by this method is the actual condensation point of pure flue gases and exceeds that based on the water vapor content of the gases because of the presence of SO_3. No great concentration of the trioxide is required to raise the dew-point over a considerable range.

(2) The formation of a film of sulphuric acid on the metal depends directly upon the temperature of the metal, and only indirectly upon the temperature either of the flue gases or of the air. The temperature of the gases may be far above the dew-point and that of the metal may still be below the condensation temperature due to the cooling effect of water or air in the economizer or preheater, respectively.

(3) The existence of hygroscopic material (i.e., material for which the saturated solution has a lower vapor pressure than the vapor pressure of water and sulphuric acid in the surrounding gases) on the surface of the metal will cause the formation of a moist film at temperatures even above the dew-point of the pure gases. It will be shown later that just this state of affairs is present in the economizers and

preheaters because of the existence of flue dust deposits and corrosion products containing hygroscopic iron sulphate.

D. Combustion of Sulphur Forms in Coal

16. *Decomposition and Oxidation of Pyrite.*—Sufficient data are now at hand to permit some conclusions to be drawn as to the reactions which the sulphur undergoes in the combustion process. It is known that sulphur exists in three forms in coal,* viz., (a) pyritic sulphur, or sulphur combined with iron, usually in the form of pyrite or marcasite, and having the chemical formula FeS_2, (b) organic sulphur, in which the sulphur is combined with carbon, and for which there is no knowledge of the definite chemical composition, and (c) sulphate sulphur, or that sulphur which has been completely oxidized and is present in the form of the sulphates of iron, calcium, and aluminum. The relative amounts of the first two forms vary considerably, although for Illinois coal they are usually present to about an equal extent. The percentage of sulphate sulphur in coal is usually exceedingly small, amounting in general to less than 0.1 per cent of the total coal. In some coals, however, notably the low grade coals, there may be much more than this.

The first reaction which the pyrite undergoes in combustion is decomposition with liberation of one-half of the sulphur. Both the free sulphur and that which remains combined with the iron is then oxidized to sulphur dioxide.† The iron is, of course, converted to the oxide at the same time. The sulphur dioxide passes off as a gas. The initial combustion of the organic sulphur must for the most part yield the same gas. In the furnace, therefore, sulphur dioxide will be the principal product of the combustion of the sulphur in coal.

17. *Oxidation of Sulphur Dioxide in Flue Gases.*—It has generally been assumed that further oxidation of the sulphur dioxide occurs as the temperature of the gases decreases, i.e., in the last pass of the boiler, the economizer, the preheater, and the stack. Accordingly, the sulphur trioxide resulting from this further oxidation should reach its greatest proportion in the stack. The maximum amount of sulphur trioxide attainable at any temperature depends upon the concentra-

*S. W. Parr, and A. R. Powell, "A Study of the Forms in Which Sulphur Occurs in Coal," Univ. of Ill., Eng. Exp. Sta. Bul. 111, 1919.

†Fichter and Schaffner, "Sulphur Evolution from Iron Pyrites," Helv. chim. acta., vol. 3, p. 869, 1920.

Thompson and Tilling, "Desulphurization of Iron Pyrites," Jour. Soc. Chem. Ind., vol. 43, p. 37, 1924.

Huttig and Lurmann, "Reactions in Pyrite Roasting," Z. angew. Chem., vol. 39, p. 759, 1926.

tions of sulphur dioxide and of oxygen. The ratio of partial pressures of sulphur trioxide and sulphur dioxide is expressed by

$$\frac{p_{SO_3}}{p_{SO_2}} = K\sqrt{p_{O_2}} \qquad (1)$$

where K is a constant that depends only on the temperature, and p_{SO_3}, etc. = partial pressure of SO_3,* etc., in atmospheres. The values of K as determined by Bodenstein and Pohl† may be expressed by the equation:

$$\log K = \frac{4.927}{T} - 4.657,$$

where T is the temperature in degrees Kelvin.‡ Since

$$p_{SO_3} = \frac{\text{per cent } SO_3}{100}, \text{ etc.,}$$

$$\frac{\text{per cent } SO_3}{\text{per cent } SO_2} = \frac{K}{10}\sqrt{\text{per cent } O_2}$$

In Table 12, values for the ratio $\frac{\text{per cent } SO_3}{\text{per cent } SO_2}$ and for the per cent sulphur present as sulphur trioxide for gases containing 5 per cent oxygen at various temperatures are shown. Evidently the extent of oxidation of sulphur dioxide should greatly increase between the temperature of 1500 and 500 deg. F. The values in the third column in the table represent the maximum percentage of the sulphur that can exist as sulphur trioxide in equilibrium in the gases for the given temperature and concentration of oxygen. Whether or not this percentage of oxidation is attained depends upon whether the rate of reaction between sulphur dioxide and oxygen is relatively great compared to the velocity of the gases in passing the points corresponding to these temperatures. The rate of this reaction is greatly affected by the presence of certain substances, known as catalysts, which speed up the reaction without being permanently changed themselves. Because some of the substances that exist in flue dust and in slag may have catalytic properties for this reaction an investigation of the rate

*The partial pressure of a component of a gas is the pressure exerted by this component. The total pressure is, of course, equal to the sum of the partial pressures of the individual components.

†Bodenstein and Pohl, Z. Elektrochem., vol. 11, p. 373, 1905; cf. Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," p. 550, McGraw-Hill Book Co., New York, 1923.

‡Deg. C. + 273.

TABLE 12
EQUILIBRIUM VALUES IN OXIDATION OF SULPHUR DIOXIDE FOR GASES CONTAINING 5 PER CENT OXYGEN AT VARIOUS TEMPERATURES

Temperature deg. F.	Ratio: $\frac{\text{Per cent } SO_3}{\text{Per cent } SO_2}$	Per cent S as SO_3
3000	0.00179	0.179
2500	0.00514	0.512
2000	0.0200	1.961
1500	0.1681	14.41
1000	5.95	85.61
500	865	99.99
250	1.58×10^9	100.00

TABLE 13
OXIDATION OF SULPHUR DIOXIDE BY AIR IN THE PRESENCE OF FLUE DUST FROM NO. 6 ILLINOIS COAL

Source of Flue Dust	Condition of Gases	Per cent SO_2 in Gases	Temperature deg. F.	Per cent Oxidation
Stoker fired boiler	Dry	0.428	169	0.00
Stoker fired boiler	Dry	0.428	221	0.195
Stoker fired boiler	Dry	0.428	313	0.233
Stoker fired boiler	Dry	0.428	399	0.312
Stoker fired boiler	Dry	0.428	485	0.799
Stoker fired boiler	Dry	0.428	578	0.518
Stoker fired boiler	Dry	0.428	668	1.234
Stoker fired boiler	Dry	0.428	754	1.782
Stoker fired boiler	Dry	0.428	844	1.266
Stoker fired boiler	Dry	0.428	925	0.111
Stoker fired boiler	Dry	0.428	1030	0.000
Stoker fired boiler	Moist	0.428	412	0.376
Stoker fired boiler	Moist	0.428	578	0.407
Stoker fired boiler	Moist	0.428	718	0.109
Stoker fired boiler	Moist	0.428	747	0.421
Stoker fired boiler	Moist	0.428	796	1.340
Pulverized fuel boiler	Dry	0.467	500	0.00
Pulverized fuel boiler	Dry	0.486	825	0.00
Pulverized fuel boiler	Moist	0.428	212	1.34
Pulverized fuel boiler	Moist	0.428	212	0.82
Pulverized fuel boiler	Moist	0.428	400	1.53

of oxidation of sulphur dioxide in the presence of flue dust was undertaken. The apparatus used for this study was similar to that used by Holmes, Ramsay, and Elder* in their study of platinized silica gels as catalysts for the oxidation of sulphur dioxide. The method of analysis of the gases was that described in Appendix A. The results are given in Table 13.† The flue dusts used as catalysts were collected from the economizers of plants A and J, and represent the ash from No. 6 Illinois coal burned on a stoker and as pulverized fuel, respectively.

*H. N. Holmes, J. Ramsay and A. L. Elder, Ind. Eng. Chem., vol. 21, p. 850, 1929.

†The author is indebted to Mr. L. F. Dobry for the experimental work on the oxidation of sulphur dioxide in the presence of flue dust.

This comparison was made because it was apparent from the analyses of the flue gases at these two plants that a smaller percentage of the sulphur exists as sulphur trioxide in the gases from pulverized coal than in the gases from the same coal when burned on a stoker.

The conditions used in the catalysis experiments were similar to those existing in actual flue gases, except that air was used as a source of oxygen, and also, in a part of the experiment, dry gases were used instead of those containing moisture. The latter expedient was necessary because the results obtained with moisture were not reproducible, evidently because of absorption of sulphuric acid by the flue dust. The rate of flow of gas per unit weight of ash was comparable to that in the economizer and preheater.

The results may be summarized as follows:

(1) The flue dust from Illinois No. 6 coal burned either on a stoker or as pulverized fuel has a small catalytic action in the oxidation of sulphur dioxide to sulphur trioxide.

(2) The maximum conversion, which amounts to approximately 2 per cent, takes place at approximately 750 deg. F. At temperatures above and below this point the rate of oxidation falls off rapidly.

In view of these results, which agree closely with those obtained in the study of the actual flue gases at plants A, C, H, and J, it is believed that the higher percentages of sulphur existing as the trioxide in the gases at plant I, where acid petroleum residues are burned, are due to undecomposed trioxide from the sulphuric acid in the fuel. Even when fuel oil containing only a small amount of acid was burned at this plant the high values for the percentage of sulphur as trioxide might well have resulted from the trioxide liberated from the ash and slag, which was absorbed when the concentration of this gas was high.

In addition to the catalytic action of the flue dust, there is another condition prevalent in the economizers and preheaters that probably bears a more important relation than any other to the formation of sulphuric acid from the sulphur dioxide, and thus to the cause of the corrosion. Ralston, Leaver, Thurston, and others* have shown that *solutions of ferric sulphate* act as powerful catalysts for the conversion of sulphur dioxide to sulphuric acid. In passing mixtures of various percentages of air and sulphur dioxide through solutions of ferrous

*E. S. Leaver and R. V. Thurston, "Ferric Sulphate and Sulphuric Acid from Sulphur Dioxide and Air," Repts. of Investigations, Serial 2556, Bureau of Mines, Dec. 1923.

G. L. Oldright, H. E. Keyes, and F. S. Wartman, "Production of Ferric Sulphate and Sulphuric Acid from Roaster Gas," Trans. Am. Inst. Min. Met. Eng., vol. 73, p. 84, 1926.

O. C. Ralston, and C. G. Maier, "The Ferric Sulphate-Sulphuric Acid Process," Bull. 260. Bureau of Mines, 1927.

F. S. Wartman and H. E. Keyes, "Development of Some Fundamentals in the Ferric Sulphate-Sulphuric Acid Process," Repts. of Investigations, Serial 2839, Bureau of Mines, Nov. 1927.

sulphate, they found that the latter was almost quantitatively converted to ferric sulphate and, after this conversion, the sulphur dioxide continued to be absorbed, forming concentrations as high as 18 per cent sulphuric acid. These experiments were repeated by the author, using gases containing 0.325 per cent sulphur dioxide and a solution of 1.5 per cent ferric sulphate. The absorption of sulphur dioxide was approximately 95 per cent with complete conversion to sulphuric acid. In view of the existence of large percentages of ferric sulphate in the deposits in the preheater and economizers the following important conclusions may be drawn for the oxidation of sulphur dioxide:

(1) A slight oxidation of sulphur dioxide takes place at high temperatures due to the catalytic action of flue dust.

(2) The greatest oxidation of the dioxide takes place on a surface covered with a moist layer of saturated ferric sulphate. The conversion to sulphuric acid is rapid, and such a layer must contain high concentrations of acid at all times.

(3) The action of both sulphuric acid and of solutions of ferric sulphate on iron or steel produces ferrous sulphate which may be immediately converted to ferric sulphate by the action of flue gases containing sulphur dioxide.

(4) Sulphur dioxide plays a part in the corrosion process, therefore, by being converted to sulphuric acid by saturated solutions of the hygroscopic ferric sulphate.

18. *Decomposition of Sulphates during Combustion.*—So far in this discussion of the reactions of sulphur in coal during combustion no mention has been made of the sulphate sulphur. These compounds exist to such a small extent in coal that little attention is paid to them by most workers. This is perhaps unfortunate as, particularly in storage coal, and in some of the lower grades of coal fresh from the mine, the sulphate sulphur may be sufficient to cause corrosion damage. At the beginning of this investigation it was pointed out* that the small percentages of sulphur trioxide in flue gases may be entirely accounted for by assuming that it is a product of the decomposition of the sulphates in the coal, and that no oxidation of the dioxide takes place. Some weight was given to this argument by the constancy of the sulphur trioxide values obtained throughout the boiler, economizer, and preheater. Furthermore, it was found that the temperatures at which these sulphates decompose come well within the tempera-

*Circular No. 20, *loc. cit.*, p. 17.

tures encountered in a boiler furnace. Thus, Hofmann* has shown that pure calcium sulphate (gypsum) begins to decompose at 1200 deg. C. (2192 deg. F.), and in the presence of silica, alumina, or ferric oxide decomposition takes place at 1000 deg. C. (1832 deg. F.). Most of the sulphate in coal is combined with the oxides of iron as ferrous and ferric sulphate. These compounds decompose at much lower temperatures, viz., 167 and 492 deg. C. (333 and 918 deg. F.), respectively. The thermal decompositions of these sulphates yield, in all cases, sulphur trioxide and the oxide of the metal.

In addition to the thermal decompositions, the sulphates undergo reduction to the sulphide by hot carbon. The subsequent oxidation of the sulphide is similar to that described for pyritic sulphur. The extent of the reduction of the sulphates in a given coal will depend upon the accessibility of the carbon to the sulphate. That is, if the sulphate exists in large particles, the opportunity for reaction with the carbon is much less than if it were finely disseminated. The distribution of the sulphate, on the other hand, would have little effect on the decomposition since no other substance is required for this reaction. The possibility that the sulphates in coal contribute some of the sulphur trioxide exists, therefore, and a higher dew-point and more severe corrosion may be expected from certain low grade coals and coal that has been in storage for several years. Table 14 shows the distribution of the three forms of sulphur in various coals.

E. Composition of Fly Ash and Deposits

19. *Analyses of Fly Ash and Deposits.*—Besides the character of gases themselves, the other factor which may enter into the external corrosion of economizers and preheaters is the type of deposit which results from the adherence on the metal of the solid particles carried by the gas stream. Solids in general do not cause corrosion except when the conditions are such that a liquid film may exist and a solution of some of the constituents of the solid is actually formed on the metal. It has been shown that such a liquid film may be formed in equilibrium with the flue gases at temperatures as high as 300 deg. F. In order to find what substances may be carried into solution by the formation of the liquid film, analyses were made of the deposits found on the economizers and preheaters of the various plants in-

*Hofmann and Mustowitsch, Trans. Am. Inst. Min. Eng., vol. 39, p. 639, 1908.
Hofmann and Wanjukow, *ibid.*, vol. 933, p. 941, 1912.
cf. also, Zawadski, Konarzavski, *et al*, Roczniki chem., vol. 6, p. 120, 1926.
Marchal, J. chim. phys. vol. 22, p. 559, 1925; vol. 23, p. 38, 1926.
Bhatt and Watson, Jour. Indian. Inst. Sci., vol. 10A, p. 117.

TABLE 14
DISTRIBUTION OF FORMS OF SULPHUR IN VARIOUS COALS

Location of Mine	Coal Bed	Sulphate Sulphur	Pyritic Sulphur	Organic Sulphur	Reference
Butler Co., Pa.	Upper Freeport	0.07	0.47	0.62	
Allegheny Co., Pa.	Pittsburgh	0.23	0.79	0.66	A. R. Powell,
McDowell Co., W. Va.	Pocahontas No. 3	0.01	0.08	0.46	Ind. Eng.
Letcher Co., Ky.	Elkhorn	0.04	0.13	0.51	Chem.,vol.12,
Morgan Co., Tenn.	Coal Creek	0.71	1.75	1.78	p. 889, 1920*
Cherokee Co., Kans.	Cherokee	0.32	1.99	0.71	
Union Co., Ky.	No. 9	0.00	1.65	1.81	
Webster Co., Ky.	No. 12	0.00	0.70	0.78	H. F. Yancey
Pike Co., Ky.	Freeburn	0.00	0.13	0.33	and Thomas
White Co., Tenn.	Sewanee	0.11	3.59	1 17	Fraser, Univ.
Greene Co., Ind.	No. 4	0.00	0.89	0.77	of Ill. Eng.
Williamson Co., Ill.	No. 6	0.00	1.04	0.79	Exp. Sta.
Franklin Co., Ill.	No. 6	0.00	1.99	1.30	Bul. 125,
Clearfield Co., Pa.	C and D	0.00	2.82	0.74	p. 53, 1924.
Franklin Co., Ill.	No. 6	0.00	1.50	1.02	
Franklin Co., Ill.	No. 6	0.00	0.81	0.69	
Union Co., Ky.	No. 9	0.00	1.05	2.23	
Boone Co., Ky.	Eagle	0.00	1.47	1.01	H. F. Yancey
Walker Co., Ala.	Pratt	0.00	0.81	0.81	and S. W.
Jefferson Co., Ala.	Pratt	0.03	0.97	0.72	Parr, Ind.
Jefferson Co., Ala.	Mary Lee	0.03	0.33	0.69	Eng. Chem.,
Clay Co., Ind.	No. 3	0.00	2.13	1.79	vol. 16,
Cummock, N. C.	Deep River	0.00	1.52	0.80	p. 508, 1924.
Cummock, N. C.	Deep River	0.00	1.53	0.55	
Bureau Co., Ill.	No. 5	0.038	5.30	1.42	
Franklin Co., Ill.	No. 6	0.009	0.48	0.61	
Franklin Co., Ill.	No. 6	0.014	0.90	0.65	
Franklin Co., Ill.	No. 6	0.006	0.67	0.45	
Franklin Co., Ill.	No. 6	0.003	0.15	0.53	
Franklin Co., Ill.	No. 6	0.005	0.33	0.55	
Franklin Co., Ill.	No. 6	0.009	0.57	0.36	
Macoupin Co., Ill.	No. 6	0.054	2.37	2.59	Ill. Geological
Macoupin Co., Ill.	No. 6	0.034	2.49	2.45	Survey†
Macoupin Co., Ill.	No. 6	0.055	2.70	2.43	
Macoupin Co., Ill.	No. 6	0.032	2.23	2.38	
Saline Co., Ill.	No. 5	0.057	1.81	0.79	
Sangamon Co., Ill.	No. 5	0.068	2.70	2.09	
Sangamon Co., Ill.	No. 5	0.049	2.67	2.10	
Vermilion Co., Ill.	.....	0.026	1.45	1.64	
Vermilion Co., Ill.	.....	0.15	3.14	1.96	
Williamson Co., Ill.	No. 6	0.012	0.73	0.47	
Williamson Co., Ill.	No. 6	0.057	0.98	0.51	
Williamson Co., Ill.	No. 6	0.042	1.08	0.43	
Williamson Co., Ill.	No. 6	0.008	1.20	0.52	
Christian Co., Ill.	No. 6	0.059	2.73	1.98	
Christian Co., Ill.	No. 6	0.054	2.81	2.14	
Christian Co., Ill.	No. 6	0.002	3.17	1.88	
Dallas Co., Ia.	.....	0.24	5.03	0.72	
Warren Co., Ia.	.....	0.28	4.96	1.88	
Polk Co., Ia.	.....	0.23	4.81	0.96	
Polk Co., Ia.	.....	0.25	4.39	0.81	

*These samples had stood some time after being taken from the mine and before analysis.
†Private communication. Published by permission of the Illinois Geological Survey. All samples were taken fresh from the mine and analyzed within one month.

cluded in the investigation. Besides the deposits, which usually exist in the form of a hard scale, samples of the fly ash which accumulates in the corners of the construction and in the soot hoppers were also analyzed.

TABLE 15
COMPOSITION OF FLY ASH AND DEPOSITS

Plant	Type	Source	Moisture	Ignition Loss†	Substances*					Fusion Point of Coal Ash
					Silica	Alumina	Iron Oxide	Calcium	Sulphur	
					Reported as					
			H_2O per cent	per cent	SiO_2 per cent	Al_2O_3 per cent	Fe_2O_3 per cent	CaO per cent	SO_3 per cent	deg. F.
A	Deposit	Boiler outlet	....	19.30	13.00	7.67	14.39	1.18	37.58	2000
A	Ash	Econ. outlet	2.62	17.60	23.96	10.25	25.15	2.86	16.10	
A	Slag‡	Boiler tubes	0.40	.....	29.83	11.42	37.54	3.64	11.04	
B	Deposit	Bottom tubes of econ.	5.42	40.82	18.90	5.18	15.16	2.72	24.50	2000
B	Deposit‡	Induced fan	4.10	13.39	12.82	0.64	19.22	3.21	36.20	
B	Ash	Top tubes of econ.	1.52	30.50	26.08	11.85	19.03	3.40	17.70	
B	Deposit	Economizer	3.58	40.26	16.53	16.62	6.54	2.20	28.31	
C	Ash	Econ. inlet	0.25	4.41	31.46	16.88	41.12	....	1.65	1990
C	Ash	Econ. outlet	5.20	2.86	29.22	16.78	42.70	2.80	1.86	
C	Deposit	Economizer	13.37	.....	1.92	2.09	33.91	0.60	38.50	
D	Ash	Economizer	0.23	28.35	27.54	23.04	20.76	....	1.52	
D	Deposit	Economizer	1.89	40.62	22.90	13.02	12.78	....	31.40	
E	Deposit	Economizer	5.69	21.61	25.36	0.90	25.50	1.80	39.78	
F	Ash	Economizer	0.24	18.76	33.74	10.26	30.74	....	5.57	2066
H	Ash	Econ. outlet	0.93	6.48	38.96	32.51	10.65	6.66	2.58	2160
H	Deposit	Economizer	4.08	45.92	18.10	16.24	11.94	0.66	26.39	
H	Ash	Second pass of boiler	0.37	9.08	41.78	20.58	16.61	4.72	3.40	
H	Deposit	Superheater	0.25	19.21	25.84	9.50	13.46	1.64	31.46	
I	Deposit‡	Preheater	....	30.00	.....	.....	57.00	....	8.8	
I	Deposit‡	Preheater	....	.....	.....	.....	40.00	....	48.00	

TABLE 15—(CONCLUDED)

Plant	Type	Source	Moisture	Ignition Loss†	Substances*					Fusion Point of Ash
					Silica	Alumina	Iron Oxide	Calcium	Sulphur	
					Reported as					
			H_2O per cent	per cent	SiO_2 per cent	Al_2O_3 per cent	Fe_2O_3 per cent	CaO per cent	SO_3 per cent	deg. F.
J	Deposit	Economizer	6.22	9.14	40.80	15.67	21.61	1.66	7.92	
J	Deposit	Boiler	0.19	3.51	40.83	27.33	13.11	5.28	7.71	
J	Deposit‡	Superheater	0.13	0.58	37.07	3.02	43.78	4.73	8.40	
J	Deposit‡	Boiler tubes	0.93	1.31	40.77	6.01	37.50	4.45	5.70	2000
J	Ash‡	Econ. settling chamber	3.43	4.76	18.06	14.43	43.07	10.52	2.86	
J	Deposit‡	Preheater tubes	2.10	3.10	20.13	6.03	38.86	2.94	20.52	
J	Ash‡	Induced fan inlet	1.71	5.50	32.87	4.84	44.19	6.02	2.81	
K	Ash	Economizer	0.32	7.47	41.64	19.55	19.96	....	0.47	
L	Ash‡	Economizer	....	2.77	55.31	33.43	6.00	1.03	0.08	2857
M	Ash¶	Direct from furnace gases	....	....	55.3	26.2	8.7	3.3	0.5	2210
N	Deposit	Preheater	4.21	24.55	29.93	25.90	9.64	1.72	17.09	
O	Ash	Econ. outlet	0.76	30.69	34.86	35.02	1.76	1.92	2.08	2893
O	Ash‡	Stoker	....	2.82	56.33	32.97	3.88	2.84	0.27	

*The alkali metals, sodium and potassium, in general were not determined. Their content may be considered equal to between 2 and 7 per cent Na_2O. Other constituents of the ash such as chlorine, phosphates, titanium, etc., were not determined. Magnesium also was found to exist to such a small extent that it is not reported in the table although it usually was determined.

†Loss on ignition represents the carbonaceous material as well as other volatile constituents such as sulphur trioxide present as sulphuric acid or as iron or aluminum sulphate. For an accurate comparison of the analyses, with the exception of the sulphur, the values should be reduced to a moisture- and loss-on-ignition-free basis.

‡Analyses supplied by plant testing laboratory.

¶From Bureau of Mines data.

The method used for analysis of these solid materials was that usually employed for analysis of igneous rocks. The samples were first fused with sodium carbonate and then put in solution in water. Analyses for the various ions were then made by ordinary methods. No attempt was made to separate the different forms of iron or of sulphur.

The results of the analyses are given in Table 15. They may be summarized as follows:

(1) The scale which accumulates on the surface of the metal in the economizers and preheaters usually contains a large percentage of sulphur, a part of which exists in the form of the sulphates of iron.

(2) There is no great difference in the actual composition of the scales from the various plants except that due to variations in the silica and alumina contents.

(3) In the case of the fly ash samples the sulphur is noticeably higher in the ash from the plants where corrosion exists.

(4) In general, the fusion points of the fly ash from the plants having corrosion are lower than those not having corrosion.

20. *Nature of Sulphur Compounds in Ash and Deposits.*—Since it is possible that the high sulphate content of the scale may have been produced by condensation of sulphuric acid when the temperature of the scale was below the dew-point of the gas, an attempt was made to determine in what form the sulphate existed, i.e., whether it was present as free sulphuric acid, as a sulphate of iron, as aluminum sulphate, or as calcium sulphate.

The ash and dust deposits from several plants were extracted with successive portions of boiling water until no further sulphate went into solution. That some of the sulphate in the ash was not removed by this extraction was indicated by a subsequent analysis of several samples. The results, however, indicate the concentrations of the sulphates of iron and aluminum and of free sulphuric acid in the soluble portion of the ash and deposits.

The method for separating these constituents was based on that described by Selvig and Ratcliff* for the analyses of acid mine waters. In the original method the primary acidity of the water due to sulphuric acid was determined by titration with sodium hydroxide, using methyl orange as an indicator. In order to prevent the inclusion of part of the ferric sulphate with the sulphuric acid the iron was completely converted to the ferrous form by the addition of potassium iodide to the solution previous to the titration. The liberated iodine

*Selvig and Ratcliff, Ind. Eng. Chem., vol. 14, p. 125, 1922.

was then removed by a few drops of sodium thiosulphate. After the titration for free sulphuric acid, the determination of the secondary acidity due to the sulphates of iron and aluminum was made by titration using phenolphthalein as an indicator. Selvig and Ratcliff state that the method produces results which are too high in primary acidity because of the effect of iron and aluminum salts, even though the precautions outlined are taken in the analyses. In order to eliminate the errors due to the incorrect end-point in the titrations outlined, use was made of the electrometric titration method. The electrode finally selected was one composed of antimony amalgam plated on a platinum surface.* This electrode gave reproducible results, and the time required for the attainment of equilibrium was short. All titrations were carried out in an atmosphere of nitrogen to prevent any reoxidation of the ferrous ions.

The results of the analyses of the various deposits and fly ash samples are shown in Table 16. They may be summarized as follows:

(1) Sulphate present as free sulphuric acid is usually high in the preheaters and economizers of plants having corrosion.

(2) A large part of the sulphur present in the deposits exists as iron and aluminum sulphate. These are undoubtedly formed from the fly ash itself, and are not the result of any action of sulphuric acid on the ash.

21. *Origin of Sulphates in Deposits.*—It is apparent from the data on the composition of the fly ash that the character of the solid material carried by the gases and deposited on the tubes varies considerably with the type of coal burned. The higher grade coals with small ash content produce less scale on the tubes than the lower grade coals. Furthermore, the scales deposited from the ash of higher grade coals contain more siliceous material. The fusion point of the ash is considerably higher when the silica content is large. Sherman and Rice,† in tests made at the 70th Street Station of the Cleveland Electric Illuminating Company, have shown that the iron and sulphur contents of the fly ash are much higher than that of the composite ash from the ash pit. Furthermore, the slag from the boiler tubes contains more iron than the composite ash. They interpreted this as indicating that the more fusible particles in the coal ash are those that contain the most iron and sulphur, and that these are the particles which have the greatest tendency to adhere to the tube surfaces. The data for the

*Shukoff and Awsejewitsch, Z. Elektrochem., vol. 35, p. 349, 1929.
†Sherman and Rice, *loc. cit.*, p. 1121.

TABLE 16
DISTRIBUTION OF SULPHUR IN WATER SOLUBLE PORTION OF FLY ASH AND DEPOSITS

Plant	Type	Source	Sulphur present as			
			H_2SO_4 per cent SO_3	$Al_2(SO_4)_3$ per cent SO_3	$Fe_2(SO_4)_3$ per cent SO_3	$CaSO_4$ per cent SO_3
B	Ash	Bottom of economizer	3.77	5.55	1.51	5.19
B	Ash	Top of economizer	0.36	1.17	3.50	6.60
B	Deposit	Bottom of economizer	6.33	4.72	3.37	4.17
B	Deposit	Top of economizer	0.67	4.44	8.77	8.48
C	Ash	Top of economizer	0.00	0.00	0.08	....
C	Deposit	Top of economizer	0.29	0.48	0.34	4.08
E	Deposit	Economizer	6.73	6.37	6.12	2.73
H	Deposit	Economizer outlet	6.19	5.65	2.15	2.03
J	Deposit	Economizer	0.00	0.00	0.00	7.73
K	Deposit	Economizer outlet	0.47	0.00	0.00	....
N	Deposit	Preheater outlet	2.28	2.31	3.80	4.73
O	Ash	Economizer outlet	0.00	0.02	0.34	1.74

ash analyses included in this investigation agree with the interpretation which Sherman and Rice have given. It appears, then, that the sulphur in the scale which forms on the economizer and preheater tubes comes from the sulphur in the fly ash particles. Since the decomposition points of the sulphates of iron are low compared to the temperatures through which the ash particles pass, it is not possible that the sulphur in the deposits existed as sulphates in the ash. Evidently it existed in the form of unburned sulphide in the ash particles, and this was oxidized after the particles had stuck to the tube surface.

It is to be noticed that the ash from the pulverized fuel systems is usually much lower in sulphur than that from the stoker fired systems. In this case the sulphur, like the carbon, is more completely oxidized and very little remains unburned. The chance for obtaining a high sulphate scale, therefore, is less when the coal is burned in the pulverized form than when burned on a stoker. The adherence of the deposit in the economizers and preheaters on pulverized fuel boilers is also noticeably less.

22. *Sulphides in Fly Ash.*—If the sulphur in the scale originates in the unburned pyrite in the ash, it should be possible to detect traces of sulphide sulphur in the fly ash if the sample is collected directly from the gases, and is not taken from the ash hopper or other source where it may have stood at a high temperature in contact with the flue gases. The analyses of several samples collected in this manner from the gases at plant A show that this is true. These are given in

TABLE 17
COMPOSITION OF FLY ASH COLLECTED DIRECTLY FROM FLUE GASES—PLANT A

Sample	Sulphide Sulphur per cent S	Sulphate Sulphur per cent SO_3	Iron per cent Fe_2O_3	Aluminum per cent Al_2O_3
1	0.04	17.60	22.35	7.15
2	0.04	22.99	16.97	8.83
3	0.06	13.93	22.56	8.09
4	0.04	16.06	24.55	9.80
5	0.08	11.26	23.16	10.44
6	0.082	13.82	17.72	14.54
7	0.084	10.31	17.01	13.03
8	0.101	12.83	14.13	10.93
9	0.096	11.66	16.37	10.01
10	0.068	11.25	15.26	17.44
11	0.105	9.76	14.60	13.85
12	0.117	7.95	24.68	3.50
13	0.112	10.34	21.64	6.04
14	0.061	9.19	22.76	4.48
15	0.148	9.25	17.77	5.28
16	0.087	8.08	21.32	3.72
17	0.098	12.84	24.75	6.53
18	0.114	7.61	16.53	8.75
19	0.134	11.21	14.80	9.60
Average....	0.088	12.00	19.42	9.05

Table 17. While the amount of sulphide sulphur present is small, it is sufficiently large to cause particles of the ash to adhere to hot metal surfaces. Samples of the ash from the same coal when burned in the pulverized form were collected at plant J. In this case the analyses showed that no sulphide was present.

In the case of the samples taken from plant A the oxidation of the sulphide takes place readily at room temperatures, and even when the sample is tightly stoppered in a glass bottle. The percentage of sulphide sulphur steadily decreases, therefore, until it can hardly be detected after two or three weeks. The oxidation proceeds faster at higher temperatures; therefore, the adherence of sulphide particles on the tube surfaces will be followed rapidly by oxidation and formation of the sulphate.

23. *Summary of Factors Influencing Scale Formation.*—The rate of accumulation of scale will depend upon the agglomeration point* of the ash, and the quantity of the sulphur in the scale will depend upon the incompleteness of the combustion of the particles passing up with the gases. In the case of pulverized fuel the combustion of both the carbon and the sulphur is more nearly complete and the chance

*The agglomeration point is the temperature at which the particles begin to adhere to one another. For most salts, other than silicates, this is approximately one-half the temperature of the melting point in degrees Kelvin (Deg. C. + 273). cf. Tammann and Sworykin, Z. anorg. allgem. Chem., vol. 176, p. 46, 1928.

for a sulphate scale to be formed is much less than when the coal is fired on a stoker. The conditions favoring the formation of a sulphate scale, therefore, are similar to those which produce smoke. The part which such deposits play in the corrosion of economizer and preheater tubes will be shown in a later section of this bulletin.

III. Prevention of Corrosion of Power Plant Equipment by Flue Gases

The conditions prevalent in flue gases that cause corrosion have been discussed in Chapter II. It should be emphasized that corrosion is a result of reactions that are brought about by numerous conditions or combinations of conditions. The change of any one condition, therefore, may not prove to prevent deterioration unless that condition happens to be the factor controlling the rate of corrosion. It is impossible to prescribe a general remedy for the corrosion of all power plant equipment because the conditions of operation, fuel, design, etc., vary greatly from one plant to another. Before the individual operator makes an attempt to reduce the destructive action of flue gases he should study the conditions in his particular plant to find which may be the cause of the damage. The remedy then may be found to lie in the choice of a different fuel, a change in operation or design, the use of protective coatings, the use of non-corroding material for construction, the processing of fuel before burning, or many of the other methods and devices used to combat corrosion.

In the course of this investigation numerous tests were made in an effort to determine which of the conditions prevalent in the flue gases cause the worst damage. These tests will be discussed in Chapter IV. The conclusion reached was that a combination of a high dew-point, and a scale containing ferric sulphate is more destructive to ordinary steel than any other condition. Even the corrosion by a spray of sulphuric acid on the metal is small compared to that caused by the combined oxidizing and acidic action of a moist film of ferric sulphate.

After a consideration of the causes of the corrosion a few general methods of reducing the loss may be described.

A. Construction and Operation of Economizers and Preheaters

24. *Minimum Operating Temperatures.*—As pointed out in Chapter II, the formation of a film of sulphuric acid on the metal surfaces in economizers and preheaters depends upon the temperature of the

metal and not upon the temperature either of the flue gases or of the water or air. In economizers it has been found that the metal temperature averages about 10 deg. F. above the temperature of the entering water at the cold end and about 40 deg. F. above the temperature of the exit water at the hot end. Proportional values evidently prevail at intermediate points. These values were obtained by peening thermocouple junctions into the surface of economizer tubes. They represent temperature differences for clean metal surfaces. When dust deposits cover the surface the temperature is closer to that of the water.

In a similar way the surface temperature of clean preheater tubes was found to be approximately the mean temperature of the gas and air at the cold end and about 20 deg. F. nearer the temperature of the air than that of the gas at the hot end. In a preheater, especially, the effect of dust deposits is noticeable and the metal temperature is much lower under this condition. It is possible, therefore, that, while a clean preheater may be operated entirely above the condensation temperature of the gases, condensation and corrosion will take place when dust collects in corners and pockets of the construction. A diffusion of gas to the metal will take place even when a thick deposit exists on the surface. In the design of preheaters, therefore, care should be taken to get good circulation of flue gas at all parts of the construction so as to prevent the collection of dust and to secure a uniform temperature gradient. This is particularly true in the plate type of preheater, where the corners are apt to be out of the main gas stream. Because of the difficulties in cleaning the plate type of preheater a non-uniform flow of gas is often the cause of severe corrosion.

Tubular preheaters also become partially clogged in spite of a fairly uniform flow of gas. It has been observed that corrosion is always severe in the clogged tubes. As stated in the preceding chapter, the tendency to clog seems to be worse in preheaters of stoker-fired boilers than in those of pulverized fuel boilers. Even when petroleum residues are burned clogging of the preheater may take place. This may be produced by certain combinations of fuels which give an undesirable type of ash, or even by the product of corrosion when the action is severe.

The minimum operating temperatures of preheaters and economizers will be determined by the type of flue dust deposit and the maximum dew-point of the gas. If the deposit is of a hygroscopic nature it may become moist at temperatures as much as 50 to 75 deg.

F. above the dew-point of the gases. In some plants a temperature of 275 deg. F. is necessary to insure against corrosion while in others no corrosion takes place at 150 deg. F. At the present time a determination of the vapor pressure of saturated solutions (hygroscopicity) of substances present in flue dust is being made in order that the minimum operating temperature may be foretold. Until definite information is obtained a practical method of establishing this temperature is to make a survey of the temperature of the metal surfaces in the preheater and economizer and compare these temperatures with the extent of the corrosion. This survey should be extended over all operating conditions encountered in the boiler as condensation may take place only when the boiler is operating at low rates of evaporation.

In general the most severe corrosion takes place in front of the air intake of the preheater. Use of recirculated hot air or of the parallel flow principle to raise the metal temperature will overcome this difficulty. Either of these, of course, will decrease the capacity of the preheater. A non-corrosive alloy may also be used in this part of the construction.

25. *Elimination of Leaks in Economizers.*—Probably the greatest step that can be taken to eliminate the local corrosion that has been found to exist in more or less severity in all plants is the elimination of leaks in the economizers. This applies particularly to leaks around the tube ends. New features in the design of economizers in the last few years have done much to meet this condition. The exact process of the development of a leak through a rolled joint seems worthy of consideration. That some peculiar conditions are at work is indicated by the fact that from 80 to 90 per cent of the leaks in the boiler system are encountered in the economizers, even though the construction in the economizer may be similar to that in the boiler proper. Whether these are brought about by greater temperature changes or by some factor which is present at the lower temperatures that is not present at the higher temperatures remains to be seen. The process of the development of a leak suggested in Chapter II is based on the experience of power plant operators. It has been observed that joints that are absolutely water tight at the beginning apparently hold longer than those that show minute seepage.* The character of the deposit from the flue dust also probably has something to do with the development of leaks. In general, plants using the higher grades of coal have not

*Serial Report of Prime Movers Committee, Boilers, Superheaters and Economizers. National Electric Light Association, Publication No. 267-33; pp. 43-4, 1927.

experienced as much trouble as those using the lower grade coals. Elimination of strains due to incoming cold water meeting hot zones, redesign of circulation systems, and changes in the baffling in the economizer will aid in decreasing the leakage.

26. *Non-Corroding Alloys.*—Under certain conditions a reduction in corrosion by any of the changes outlined is obviously impossible. For instance, the corrosion of fan blades may be difficult to control under any condition. Also the economic loss involved in maintaining a high minimum preheater metal temperature may be such that the change is not warranted for some types of fuels. In such cases the obvious solution is the use of non-corroding alloys which withstand the action of the corrosive conditions. While the original cost of the alloys is somewhat higher than that of steel, the greater life and dependability will often more than compensate for the greater original investment.

In connection with this investigation some 56 alloys of various compositions, 16 paints, and several enamel coatings were tested for their resistance to corrosion. These tests were made in four ways, viz., (a) an accelerated test in which the samples were immersed in aerated solutions of 36 and 50 per cent sulphuric acid at 200 deg. F., (b) an accelerated test in aerated solutions of 36 and 50 per cent sulphuric acid saturated with ferric sulphate at 200 deg. F., (c) a slow test in which the samples were suspended in flue gas (from the combustion of city gas) of constant composition, to which were added sulphur dioxide gas and sulphuric acid vapor, maintained at 200 deg. F., (d) samples covered with solid ferric sulphate exposed to the same gases as in (c). A more complete description of these tests, as well as others made on corrosion, will be found in Chapter IV.

The results of the corrosion tests may be summarized as follows:

(1) The corrosion of pure iron is greatly accelerated by the presence of ferric sulphate.

(2) The presence of small amounts of copper, nickel, molybdenum, silicon, carbon, manganese, phosphorus, or sulphur in iron or steel does not noticeably affect the rate of corrosion by flue gases.

(3) Chromium steels are attacked rapidly by pure acid, but in the presence of ferric sulphate they are rendered entirely passive and the attack is not noticeable. The maximum protection is afforded by the presence of between 14 and 30 per cent chromium.

(4) The addition of nickel to chromium steels does not decrease the corrosion resistance until more than 20 per cent has been added.

The type of alloy known as "18-8 stainless iron" offers excellent resistance to flue gases.

(5) Chromium-nickel alloys containing more than 20 per cent each of chromium and nickel do not offer as much resistance as the stainless irons.

(6) Copper alloys in general are rapidly attacked by the action of ferric sulphate, the corrosion being several times that produced by pure sulphuric acid. It is interesting to note that copper-steel is no more resistant to the conditions encountered than is ordinary steel.

(7) Pure lead and antimonial lead are attacked by the action of flue gases at 200 deg. F. (see Fig. 5). This emphasizes the fact that the concentration of sulphuric acid condensing from the gases at 200 deg. is high. Calculations from vapor pressure data indicate that the acid is between 65 and 80 per cent sulphuric acid.

(8) No paints were found that were absolutely resistant to the action of the hot gases. A few of the artificial phenol resins seemed to provide good protection.

B. Preparation of Coal by Removal of Ash and Sulphur

27. *Introduction.*—In the preceding chapter the total sulphur content of the coal has been shown to be responsible for the corrosion conditions in flue gases. While only a small part of the sulphur is converted to sulphuric acid, the fraction converted is dependent upon the concentration of sulphur dioxide in the gases. The sulphide particles carried up by the gases were also found to be responsible for slagging and scale formation in the preheater and economizer. Since approximately 60 per cent of the sulphur in most coals is combined with the ash-forming constituents, it is obvious that any method of removing the sulphur must also produce beneficial results in the decrease of ash.

The advantages of washing coal have been so thoroughly covered by other investigators* that is is unnecessary to discuss them here.

*A. W. Belden, G. R. Delamater, J. W. Groves, and K. M. Way, "Washing and Coking Tests of Coal at the Fuel-Testing Plant at Denver, Colo." Bul. 5, Bureau of Mines, 1910.
L. W. Lord, "Experimental Work Conducted in the Chemical Laboratory of United States Fuel-Testing Plant at St. Louis, Mo.," Bul. 28, Bureau of Mines, 1911.
F. C. Lincoln, "Coal Washing in Illinois," Univ. of Ill. Eng. Exp. Sta. Bul. 69, 1913.
David Hancock, "Coal Washing in Alabama;" "Iron Making in Alabama;" Geological Survey of Alabama, 3d ed., 1912.
T. J. Drakeley, "Coal Washing—A Scientific Study," Trans. Inst. Min. Eng., vol. 54, p. 418, 1917; vol. 59, p. 86, 1919.
E. R MacMillan and B. M. Bird, "Coal-Washing Problems of the Pacific Northwest," Univ. of Wash. Eng. Exp. Sta. Bul. 28, 1924.
W. R. Chapman and R. A. Mott, "The Cleaning of Coal," Fuel in Science and Practice, vol. 5, p. 143, 1926, *et seq.*
H. F. Yancey and Thomas Fraser, "Coal-Washing Investigations," Bul. 300, Bureau of Mines, 1929.
A. C. Callen and D. R. Mitchell, "Washability Tests of Illinois Coals," Univ. of Ill. Eng. Exp. Sta. Bul. 217, 1930.

The deleterious effects of the impurities in coal, besides corrosion, may be enumerated briefly: (1) more difficult combustion, due to the dilution of the combustible portion of the coal, (2) increased cost of handling due to the handling of worthless material with the coal in the various steps of its distribution and utilization, (3) greater heat loss in the furnace due to the combustible in the ash, to the requirement of larger percentages of excess air for combustion and to the sensible heat lost in the grate refuse, (4) greater heat loss in the boiler due to the slagging of tubes, (5) damage to furnace walls, and (6) liability to spontaneous heating of stored coal, which probably has a relationship to the sulphur content.

The fact that many advantages are to be gained by cleaning coal makes it surprising that the operation has not been adopted more extensively than it has. Yancey and Fraser* state that in 1927 approximately 22 million tons of coal were washed in the United States, an equivalence of 3.8 per cent of the total output. Of this quantity, fourteen and one-half million tons were washed in the State of Alabama alone where a large proportion of this fuel is used for the manufacture of iron and steel. In Illinois, Indiana, Ohio, West Virginia, Pennsylvania, and Kentucky less than 2 per cent of the total coal mined is subjected to washing operations. In Great Britain during the same year 51 million tons, or 20.5 per cent of the total output, were cleaned.

The methods used for cleaning coal for the most part depend upon the difference in the specific gravities of pure coal and that of ash-forming constituents. Several types of washers are in use in which a moving body of water is employed to bring about the separation. These include the trough and launder washers, piston and pan jigs, rising-current classifiers, and washing tables. In addition to these, separation may be brought about by pneumatic devices, by flotation in a sand-water mixture, by flotation with froth, or by means of electrostatic or magnetic fields.

At the present state of knowledge of the composition of coal the absolute limit which any method of coal cleaning may attain is the removal of the segregated impurities that exist as more or less discrete particles in the coal at the size selected for cleaning. Finely distributed ash particles and sulphur and other inorganic elements combined with the carbon and distributed throughout the coal cannot be removed. Reference to Table 14 shows that the limit of sulphur reduction, therefore, in many cases is less than 60 per cent of the

*Loc. cit., p. 4.

total sulphur present. In view of the increasing importance of the sulphur problem in coal and of the almost entire absence of fundamental knowledge of the organic sulphur compounds it would appear that research on the nature and properties of these compounds is highly desirable.

28. *Specific Gravity Studies of Coal.*—The extent to which the ash and sulphur can be removed from coal by the present cleaning methods is usually predicted by a specific gravity analysis. For this purpose a representative sample of the coal is immersed in a liquid solution having a specific gravity intermediate between that of the coal and the impurities. The portion of the coal having a specific gravity less than that of the solution floats, while that with a greater specific gravity sinks. By the use of a series of such solutions, usually covering the range from 1.25 to 1.80 specific gravity, the coal may be separated into portions according to the density of the individual particles. In general the sulphur and ash content increases and the calorific value decreases with the specific gravity of the fractions.

Because of the large amount of data that has been published on the washability of coals from various sections of the United States it was not considered necessary to make specific gravity separations of the fuels burned at the various power plants included in this investigation in order to show the benefits that may be derived from cleaning. This subject, however, was interesting from another standpoint connected with the corrosion problem. As mentioned in Chapter II, one of the causes of corrosion is the accumulation on the metal surfaces of flue dust deposits which contain compounds of iron and sulphur. It was also shown that the particles of the ash which tend most to adhere to the metal are those that contain iron and sulphur present as iron sulphide. Although the causes of slagging in boilers and of dust deposition in economizers and preheaters have not been thoroughly investigated it seems plausible to believe that these troubles originate in the finely disseminated ash-forming particles that exist in the lower and middle specific gravity portions of the coal. Heavy particles of coal containing only a small proportion of combustible not only have difficulty in leaving the fuel bed but also lack the buoyancy of the hot sphere of gas that a particle containing more combustible possesses. Furthermore, the time required for burning two particles of the same size would be greater for the one having the greater amount of combustible. The temperature of the ash

residue at the time the particles enter the boiler would be higher for these low specific gravity particles. The tendency to adhere to the surface of tubes and walls depends upon the temperature and composition of the fly-ash particles. It is quite probable, therefore, that the accumulation of unburned iron sulphide, which is later oxidized to iron sulphate, on the surfaces of economizers and preheaters depends upon the quantity of finely disseminated pyrite in the bony portion of the coal and not on the total quantity of impurities in the coal.

In an effort to establish some relation between the tendency of flue dust to adhere to surfaces and the distribution of ash and sulphur in the coal several of the coals used as fuels in the plants investigated were separated into portions according to the specific gravity, and these portions were analyzed for moisture, ash, and sulphur. Since it is possible for only very small particles to leave the furnace bed and since the extent of crushing obviously has some effect on the separation of ash from coal, the coals studied were ground to the smallest sizes that could be used effectively in the separations. Approximately one-third of each sample was retained by a 10-mesh sieve and contained particles up to ¼ in.; one-third contained particles between 10 and 20-mesh, and the other third contained particles below 20-mesh. The coals were separated into these three fractions and each fraction was subjected to float-and-sink separation in zinc chloride solutions ranging from 1.25 to 1.80 specific gravity. On account of the small sizes employed only about 3 pounds of coal were used for each fraction and care was taken to get good separation of the float-and-sink fractions. Analyses of the samples were made in the usual way after washing, drying, and crushing to 60-mesh.

The results of the distribution study are reported in Tables 18 to 22 and in Figs. 14 and 15.

In order to bring out the differences in the ash and sulphur distribution in the various coals the results are plotted as cumulative units against the specific gravity. A cumulative unit of ash, or sulphur, may be defined as the total weight of ash or sulphur, respectively, existing in that fraction of 100 pounds of coal having a specific gravity below a given value. The values of unit ash and sulphur are obtained by multiplying the percentage of ash or sulphur in the individual specific gravity fractions by the weight of the fraction expressed as a percentage of the screen-size sample and dividing by 100.

TABLE 18

SPECIFIC GRAVITY DISTRIBUTION OF ASH AND SULPHUR IN ILLINOIS NO. 6 COAL FROM KINCAID MINE, CHRISTIAN COUNTY, ILLINOIS

Original Size—Nut
Screen Analysis
Over 10 mesh = 36.4 per cent
10 to 20 mesh = 33.1 per cent
Under 20 mesh = 30.5 per cent
Analyses Reported on Dry Basis

Specific Gravity	Yield		Ash			Sulphur		
	Per cent	Cumulative Per cent	Per cent	Cumulative Per cent	Cumulative Unit	Per cent	Cumulative Per cent	Cumulative Unit
Over 10 mesh								
Under 1.25...	21.2	21.2	6.67	6.67	1.41	3.39	3.39	0.72
1.25 to 1.30...	0.8	22.0	6.84	6.68	1.47	3.33	3.39	0.75
1.30 to 1.35...	8.6	30.6	7.96	7.04	2.15	3.62	3.45	1.06
1.35 to 1.45...	40.3	70.9	12.30	10.03	7.11	4.60	4.10	2.91
1.45 to 1.50...	11.9	82.8	19.16	11.34	9.39	6.24	4.40	3.65
1.50 to 1.60...	4.4	87.2	26.31	12.10	10.55	8.41	4.62	4.02
1.60 to 1.80...	3.7	90.9	34.83	13.02	11.83	9.09	4.79	4.36
Over 1.80.....	9.1	100.0	59.99	17.30	17.30	23.10	6.46	6.46
10 to 20 mesh								
Under 1.25...	1.9	1.9	6.73	6.73	0.13	3.25	3.25	0.06
1.25 to 1.30...	0.2	2.1	5.69	5.65	0.14	3.41	3.26	0.07
1.30 to 1.35...	36.3	38.4	6.99	6.97	2.67	3.31	3.31	1.27
1.35 to 1.40...	28.0	66.4	10.88	8.62	5.72	4.13	3.65	2.43
1.40 to 1.45...	12.6	79.0	15.42	9.71	7.67	5.08	3.88	3.07
1.45 to 1.50...	3.9	82.9	18.64	10.13	8.41	6.01	3.98	3.30
1.50 to 1.60...	7.5	90.4	22.81	11.18	10.11	7.58	4.28	3.87
1.60 to 1.80...	3.2	93.6	32.26	11.90	11.14	9.92	4.47	4.19
Over 1.80.....	6.4	100.0	60.21	14.99	14.99	21.58	5.57	5.57
Under 20 mesh								
Under 1.30...	7.9	7.9	7.10	7.10	0.56	3.87	3.87	0.31
1.30 to 1.35...	28.5	36.4	7.14	7.13	2.60	3.81	3.82	1.39
1.35 to 1.40...	21.4	57.8	8.88	7.78	4.50	4.20	3.96	2.29
1.40 to 1.45...	15.7	73.5	12.43	1.77	6.45	5.03	4.19	3.08
1.45 to 1.50...	9.0	82.5	16.89	9.66	7.97	5.89	4.38	3.61
1.50 to 1.60...	5.5	88.0	32.39	11.08	9.75	7.17	4.55	4.01
1.60 to 1.80...	3.4	91.4	23.68	11.54	10.55	9.01	4.72	4.31
Over 1.80.....	8.6	100.0	71.36	16.67	16.67	17.50	5.81	5.81

TABLE 19

SPECIFIC GRAVITY DISTRIBUTION OF ASH AND SULPHUR IN MIDDLE KITTANING COAL FROM MUSKINGUM COUNTY, OHIO

Original Size—Slack
Screen Analysis
Over 10 mesh = 38.8 per cent
10 to 20 mesh = 30.9 per cent
Under 20 mesh = 30.3 per cent
Analyses Reported on Dry Basis

Specific Gravity	Yield		Ash			Sulphur		
	Per cent	Cumulative Per cent	Per cent	Cumulative Per cent	Cumulative Unit	Per cent	Cumulative Per cent	Cumulative Unit
Over 10 mesh								
Under 1.25...	28.2	28.2	2.68	2.68	0.76	2.16	2.16	0.61
1.25 to 1.30...	37.2	65.8	4.06	2.90	1.91	2.75	2.48	1.64
1.30 to 1.35...	11.9	77.7	8.42	3.75	2.91	4.68	2.83	2.20
1.35 to 1.40...	4.9	82.6	12.97	4.29	3.55	6.76	3.06	2.53
1.40 to 1.45...	2.6	85.2	15.97	4.65	3.96	7.44	3.20	2.72
1.45 to 1.50...	1.7	86.9	16.49	4.88	4.24	8.15	3.30	2.86
1.50 to 1.60...	2.6	89.5	23.83	5.43	4.86	9.57	3.47	3.11
1.60 to 1.80...	2.0	91.5	32.43	6.02	5.51	12.22	3.67	3.36
Over 1.80.....	8.5	100.0	68.30	11.32	11.32	14.31	4.57	4.57
10 to 20 mesh								
Under 1.25...	33.3	33.3	2.41	2.41	0.80	2.23	2.23	0.74
1.25 to 1.30...	30.5	63.8	2.39	2.40	1.53	2.36	2.29	1.46
1.30 to 1.35...	14.6	78.4	5.67	3.01	2.36	3.86	2.58	2.03
1.35 to 1.40...	6.1	84.5	8.98	3.44	2.91	5.62	2.80	2.37
1.40 to 1.45...	2.5	87.0	12.27	3.69	3.21	7.44	2.94	2.55
1.45 to 1.50...	2.1	89.1	16.54	4.00	3.56	8.19	3.06	2.73
1.50 to 1.60...	2.1	91.2	21.22	4.39	4.01	9.82	3.22	2.93
1.60 to 1.80...	2.2	93.4	32.55	5.06	4.72	11.39	3.41	3.18
Over 1.80.....	6.6	100.0	65.20	9.02	9.03	15.51	4.21	4.21
Under 20 mesh								
Under 1.30...	17.1	17.1	3.13	3.13	0.54	2.60	2.60	0.45
1.30 to 1.35...	58.3	75.4	5.13	4.68	3.53	2.48	2.51	1.89
1.35 to 1.40...	7.1	82.5	11.84	5.29	4.36	4.53	2.68	2.21
1.40 to 1.45...	4.5	87.0	12.37	5.66	4.92	5.94	2.85	2.48
1.45 to 1.50...	2.0	89.0	16.21	5.90	5.25	7.50	2.96	2.63
1.50 to 1.60...	2.3	91.3	21.08	6.27	5.72	7.57	3.07	2.80
1.60 to 1.80...	2.9	94.2	31.61	7.05	6.64	12.36	3.36	3.16
Over 1.80.....	5.8	100.0	65.27	10.46	10.46	13.88	3.97	3.97

TABLE 20

SPECIFIC GRAVITY DISTRIBUTION OF ASH AND SULPHUR IN CHEROKEE COAL FROM CRAWFORD AND CHEROKEE COUNTIES, KANSAS

Original Size—Slack
Screen Analysis
Over 10 mesh = 17.4 per cent
10 to 20 mesh = 42.5 per cent
Under 20 mesh = 40.1 per cent
Analyses Reported on Dry Basis

Specific Gravity	Yield		Ash			Sulphur		
	Per cent	Cumulative Per cent	Per cent	Cumulative Per cent	Cumulative Unit	Per cent	Cumulative Per cent	Cumulative Unit
Over 10 mesh								
Under 1.25...	50.8	50.8	3.78	3.78	1.92	2.08	2.08	1.06
1.25 to 1.30...	7.2	58.0	5.85	4.04	2.34	2.69	2.16	1.25
1.30 to 1.35...	16.4	74.4	11.52	5.69	4.23	3.51	2.45	1.83
1.35 to 1.40...	6.9	81.3	10.98	6.14	4.99	5.19	2.69	2.18
1.40 to 1.45...	3.0	84.3	13.69	6.41	5.40	5.50	2.79	2.35
1.45 to 1.50...	2.0	86.3	17.61	6.66	5.75	6.07	2.86	2.47
1.50 to 1.60...	2.1	88.4	23.54	7.07	6.25	7.45	2.97	2.63
1.60 to 1.80...	1.8	90.2	35.40	7.63	6.88	8.25	3.08	2.78
Over 1.80.....	9.8	100.0	75.94	14.32	14.32	11.86	3.94	3.94
10 to 20 mesh								
Under 1.25...	59.0	59.0	3.63	3.63	2.14	2.42	2.42	1.43
1.25 to 1.30...	5.4	64.4	3.77	3.64	2.35	2.40	2.42	1.56
1.30 to 1.35...	11.2	75.6	6.40	4.05	3.06	3.20	2.53	1.92
1.35 to 1.40...	6.7	82.3	7.57	4.34	3.57	4.87	2.72	2.24
1.40 to 1.45...	3.3	85.6	7.13	4.44	3.80	5.79	2.84	2.43
1.45 to 1.50...	1.7	87.3	17.94	4.71	4.11	6.96	2.92	2.55
1.50 to 1.60...	2.0	89.3	20.58	5.06	4.52	7.76	2.99	2.67
1.60 to 1.80...	1.5	90.8	31.05	5.49	4.99	10.55	3.11	2.83
Over 1.80.....	9.2	100.0	74.59	11.85	11.85	11.88	3.92	3.92
Under 20 mesh								
Under 1.30...	1.8	1.8	5.17	5.17	0.09	2.24	2.24	0.04
1.30 to 1.35...	47.4	49.2	5.07	5.07	2.50	2.06	2.07	1.02
1.35 to 1.40...	21.0	70.2	5.43	5.18	3.64	2.85	2.30	1.62
1.40 to 1.45...	9.0	79.2	10.14	5.74	4.55	4.19	2.51	1.99
1.45 to 1.50...	5.7	84.9	13.82	6.29	5.34	5.30	2.70	2.29
1.50 to 1.60...	3.1	88.0	31.40	7.17	6.32	7.57	2.87	2.53
1.60 to 1.80...	3.3	91.3	52.09	8.82	8.06	9.49	3.12	2.85
Over 1.80.....	8.7	100.0	75.74	14.62	14.62	11.36	3.83	3.83

TABLE 21

SPECIFIC GRAVITY DISTRIBUTION OF ASH AND SULPHUR IN ILLINOIS NO. 5 COAL FROM SALINE COUNTY, ILLINOIS

Original Size—Screenings
Screen Analysis
Over 10 mesh = 61.5 per cent
10 to 20 mesh = 14.5 per cent
Under 20 mesh = 24.0 per cent
Analyses Reported on Dry Basis

Specific Gravity	Yield		Ash			Sulphur		
	Per cent	Cumulative Per cent	Per cent	Cumulative Per cent	Cumulative Unit	Per cent	Cumulative Per cent	Cumulative Unit
Over 10 mesh								
Under 1.30...	30.6	30.6	3.59	3.59	1.10	1.29	1.29	0.39
1.30 to 1.35...	32.2	62.8	6.37	5.02	3.15	1.33	1.31	0.82
1.35 to 1.40...	29.0	91.8	10.16	6.64	6.09	1.66	1.42	1.30
1.40 to 1.45...	3.2	95.0	15.23	6.93	6.58	3.38	1.49	1.41
1.45 to 1.50...	1.2	96.2	20.12	7.02	6.82	4.06	1.52	1.46
1.50 to 1.60...	1.0	97.2	25.60	7.28	7.08	6.33	1.57	1.52
1.60 to 1.80...	0.5	97.7	33.53	7.43	7.26	4.88	1.59	1.55
Over 1.80.....	2.3	100.0	64.59	8.74	8.74	14.23	1.88	1.88
10 to 20 mesh								
Under 1.30...	9.4	9.4	1.70	1.70	0.16	1.05	1.05	0.10
1.30 to 1.35...	59.3	68.7	4.87	4.44	3.05	1.27	1.24	0.85
1.35 to 1.40...	15.2	83.9	9.88	5.42	4.55	1.48	1.28	1.08
1.40 to 1.45...	5.8	89.7	13.86	5.97	5.35	1.81	1.32	1.18
1.45 to 1.50...	2.0	91.7	16.81	6.20	5.69	2.28	1.34	1.23
1.50 to 1.60...	1.5	93.2	23.79	6.49	6.05	3.35	1.38	1.28
1.60 to 1.80...	1.4	94.6	36.72	6.91	6.53	5.19	1.43	1.35
Over 1.80.....	5.5	100.0	71.35	10.46	10.46	14.71	2.16	2.16
Under 20 mesh								
Under 1.30...	7.8	7.8	3.74	3.74	0.29	1.12	1.12	0.09
1.30 to 1.35...	48.9	56.7	6.33	5.46	3.39	1.23	1.21	0.69
1.35 to 1.40...	12.9	69.6	10.85	6.88	4.79	1.24	1.22	0.85
1.40 to 1.45...	4.3	73.9	14.81	7.34	5.42	1.35	1.23	0.91
1.45 to 1.50...	5.2	79.1	14.30	7.81	6.17	1.24	1.23	0.97
1.50 to 1.60...	3.2	82.3	17.65	8.18	6.73	1.61	1.24	1.02
1.60 to 1.80...	10.9	93.2	31.27	10.88	10.14	3.63	1.52	1.42
Over 1.80.....	6.8	100.0	72.19	15.05	15.05	16.78	2.56	2.56

TABLE 22

SPECIFIC GRAVITY DISTRIBUTION OF ASH AND SULPHUR IN ILLINOIS NO. 6 COAL FROM WILLIAMSON COUNTY, ILLINOIS

Original Size—Screenings
Screen Analysis
Over 10 mesh = 54.6 per cent
10 to 20 mesh = 23.8 per cent
Under 20 mesh = 21.6 per cent
Analyses Reported on Dry Basis

Specific Gravity	Yield		Ash			Sulphur		
	Per cent	Cumulative Per cent	Per cent	Cumulative Per cent	Cumulative Unit	Per cent	Cumulative Per cent	Cumulative Unit
Over 10 mesh								
Under 1.25...	29.7	29.7	3.47	3.47	1.03	1.27	1.27	0.38
1.25 to 1.30...	29.9	59.6	6.60	5.04	3.00	2.29	1.78	1.06
1.30 to 1.35...	22.9	82.5	9.48	6.27	5.17	1.63	1.74	1.44
1.35 to 1.40...	5.7	88.2	17.79	7.02	6.19	1.58	1.73	1.53
1.40 to 1.45...	3.3	91.5	20.27	7.49	6.86	1.46	1.72	1.57
1.45 to 1.50...	2.4	93.9	24.39	7.93	7.44	1.64	1.72	1.61
1.50 to 1.60...	1.5	95.4	32.58	8.31	7.93	1.70	1.72	1.64
1.60 to 1.80...	1.6	97.0	42.44	8.88	8.61	2.06	1.72	1.67
Over 1.80.....	3.0	100.0	66.71	10.61	10.61	18.44	2.22	2.22
10 to 20 mesh								
Under 1.25...	57.9	57.9	6.37	6.37	3.69	2.02	2.02	1.17
1.25 to 1.30...	0.9	58.8	10.58	6.43	3.78	2.01	2.02	1.19
1.30 to 1.35...	10.2	69.0	11.94	7.25	5.00	1.82	1.99	1.37
1.35 to 1.40...	19.0	88.0	15.10	8.94	7.87	2.14	2.02	1.78
1.40 to 1.45...	4.7	92.7	15.00	9.25	8.58	1.92	2.02	1.87
1.45 to 1.50...	2.5	95.2	17.94	9.48	9.02	2.03	2.02	1.92
1.50 to 1.60...	0.7	95.9	22.59	9.57	9.18	2.43	2.02	1.94
1.60 to 1.80...	2.7	98.6	38.76	10.37	10.23	4.58	2.09	2.06
Over 1.80.....	1.4	100.0	63.15	11.11	11.11	17.21	2.30	2.30
Under 20 mesh								
Under 1.25...	25.6	25.6	10.38	10.38	2.65	1.44	1.44	0.37
1.25 to 1.30...	2.4	28.0	8.34	10.20	2.85	1.64	1.46	0.41
1.30 to 1.35...	49.1	77.1	9.74	9.91	7.64	1.64	1.57	1.21
1.35 to 1.40...	9.3	86.4	27.61	11.81	10.20	3.18	1.75	1.51
1.40 to 1.45...	4.6	91.0	21.77	12.31	11.20	2.43	1.77	1.61
1.45 to 1.50...	1.8	92.8	22.81	12.51	11.60	2.30	1.78	1.65
1.50 to 1.60...	1.8	94.6	25.56	12.77	12.08	2.08	1.78	1.69
1.60 to 1.80...	1.8	96.4	60.95	13.66	13.17	4.85	1.84	1.77
Over 1.80.....	3.6	100.0	75.82	15.88	15.88	6.86	2.02	2.02

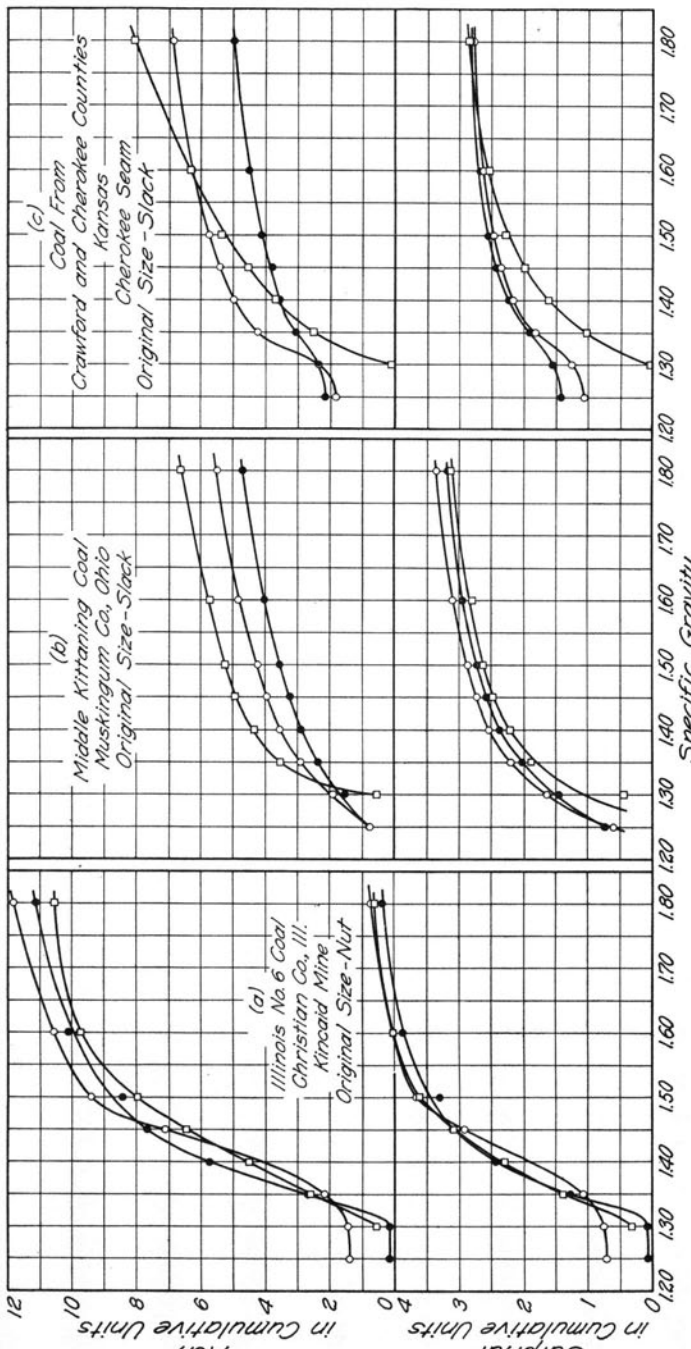


FIG. 14. SPECIFIC GRAVITY—UNIT ASH AND SULPHUR CURVES FOR COALS TESTED

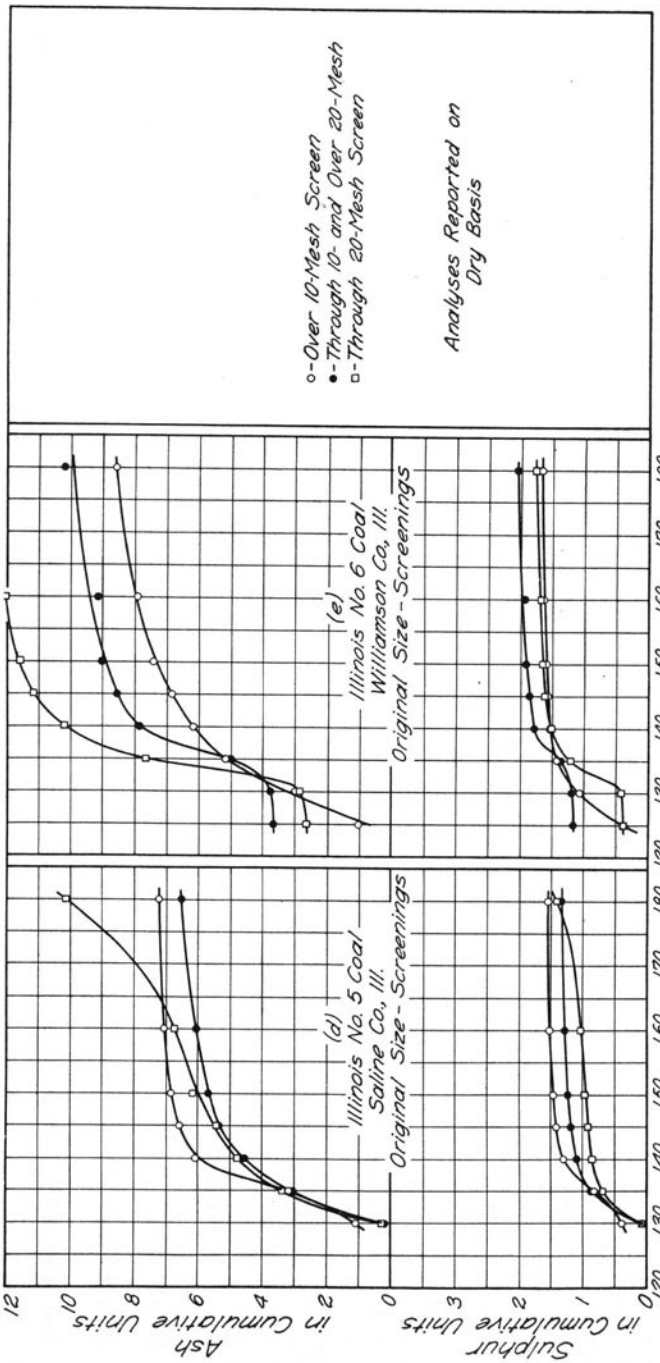


FIG. 14 (CONTINUED). SPECIFIC GRAVITY—UNIT ASH AND SULPHUR CURVES FOR COALS TESTED

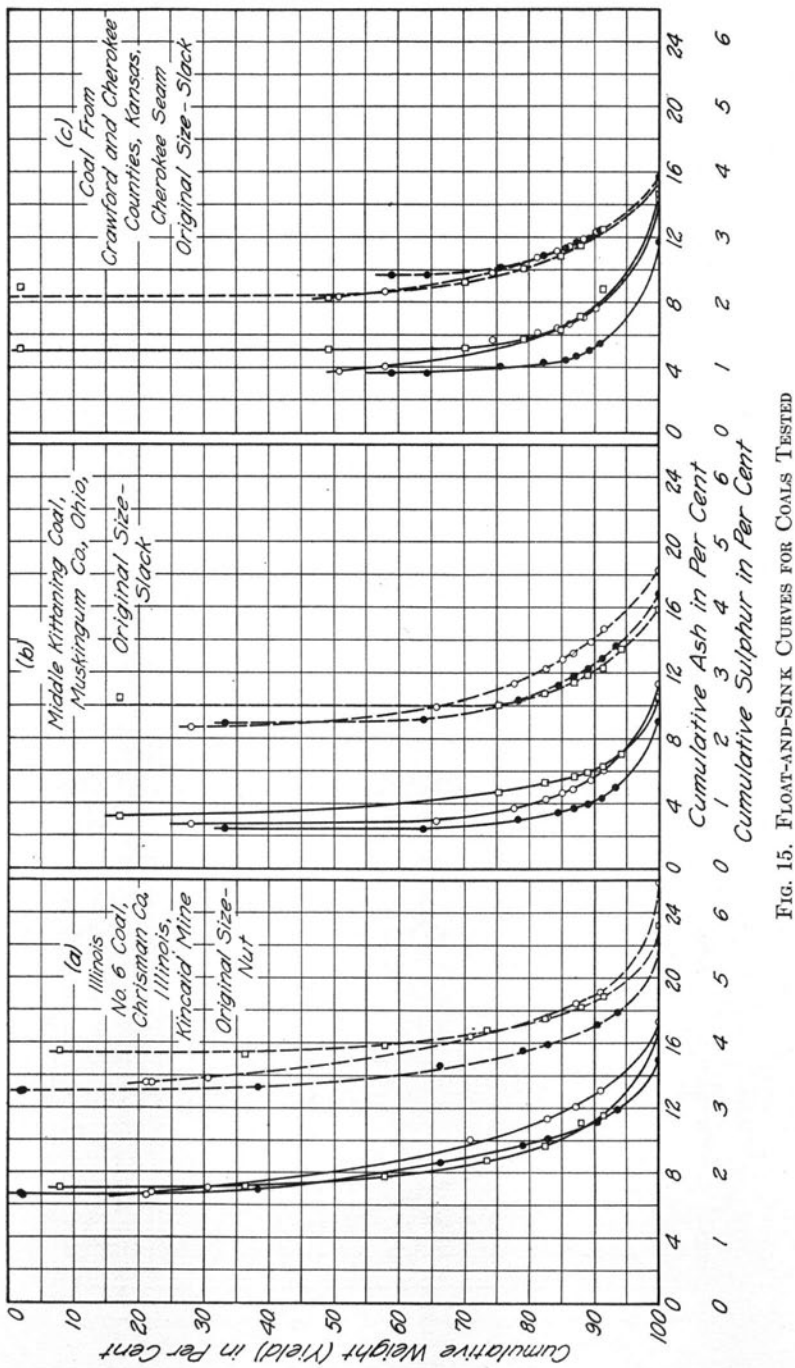


FIG. 15. FLOAT-AND-SINK CURVES FOR COALS TESTED

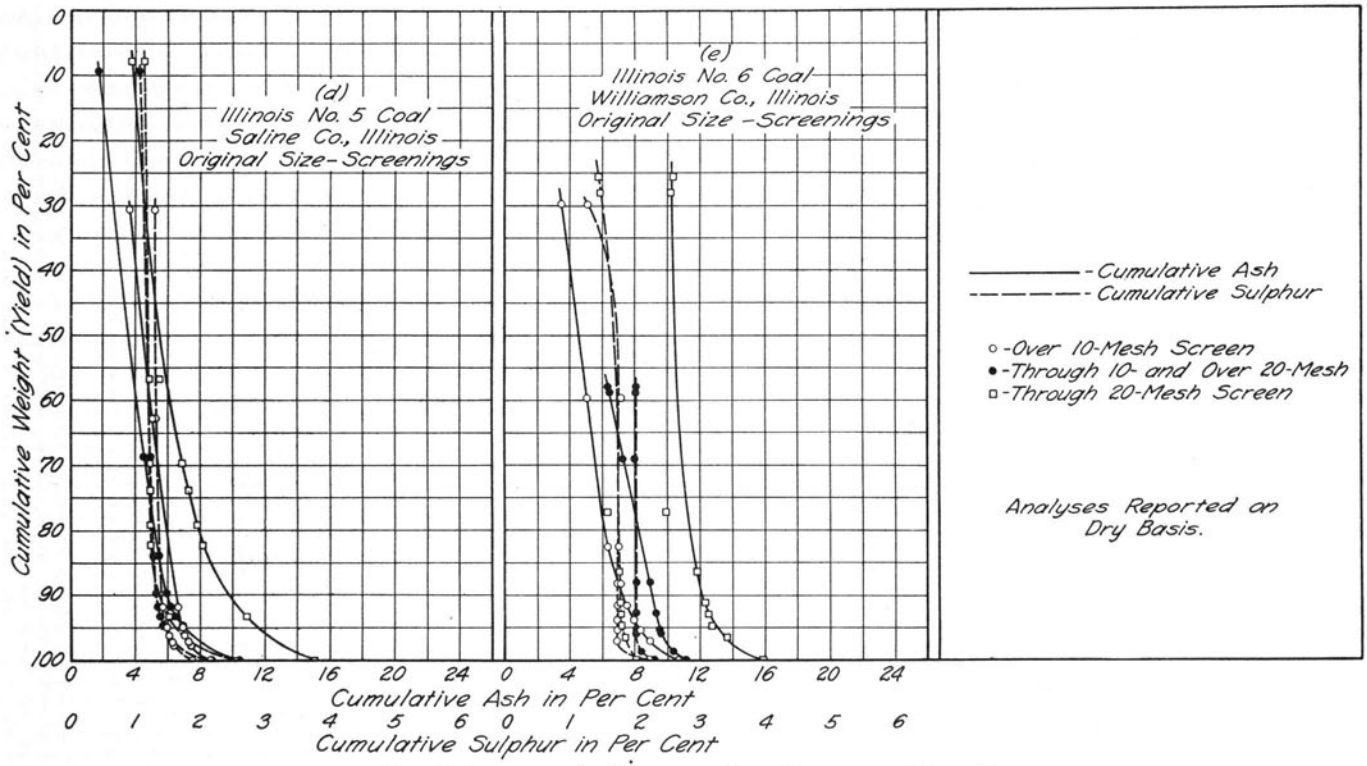


FIG. 15 (CONTINUED). FLOAT-AND-SINK CURVES FOR COALS TESTED

Of the five coals for which the distribution of ash and sulphur is reported, two produce heavy deposits in economizers and preheaters. These are the No. 6 Illinois coal from Christian Co., Ill., and the Middle Kittaning coal from Muskingum Co., Ohio. The former is burned at plants A and B and the latter at plant C. As pointed out before, these heavy deposits, high in iron sulphates, contribute to a severe general corrosion. The other coals are burned at plants where no corrosion was found and the economizers are easy to clean. While some trouble was reported in the latter plants due to slagging in the first rows of boiler tubes, the general extent of slagging was by no means as great as with the first two coals. Attention should be called to the fact that the fusing points of the ash from each of the coals selected do not vary greatly and correspond to what is generally classified as low-fusing ash.

The large amount of sulphur present in the middle portions of the coals represented in Fig. 14a and 14b corresponds to the difficulty of completely burning the particles of these coals that leave the fuel bed. The coal represented in Fig. 14e has a high ash but a much lower sulphur content in the middle specific gravity fractions.

The data obtained in the study of the distribution of ash and sulphur in coal can be used, of course, to predict the washability of these fuels. The usual method for presenting float-and-sink data is to plot the cumulative weight (yield) as a percentage of the sample against the cumulative ash and sulphur as per cent. Such curves show at a glance the limiting proportions of ash or sulphur that will be obtained when a given fraction of the coal is separated according to the specific gravity selected for the cleaning operation. Thus from Fig. 15a a reduction of ash from 16 to 12 per cent (or 25 per cent reduction) can be made in Christian Co., Illinois, coal by the removal of the heaviest 10 per cent of the raw coal. The accompanying reduction in sulphur content of this particular sample is from 6 to 4.5 per cent. The curves also show that a removal of 20 per cent of the raw coal (80 per cent yield) only reduces the ash to 10 per cent and the sulphur to about 4 per cent. An idea of the ease and efficiency of a cleaning process for a coal is given by the deviation of these float-and-sink curves from a straight line tangent to the upper portion of the curve.* Such a line would indicate uniform distribution of ash, or sulphur, and separation of the impurities would be impossible. The sharper the angle which the curve makes near the abscissa the more

*See "Interpretation of Float-and-Sink Data" by B. M. Bird, Proc. of Second International Conference on Bituminous Coal, vol. 2, p. 82, Carnegie Inst. of Technology, Pittsburgh, 1928, for a discussion of a more elaborate method of interpretation of these data.

marked is the increase in ash content of the coal at this point. It is to be noted that a substantial decrease in ash and sulphur content may be brought about by washing any of the coals studied, with the exception of the particular one from Williamson Co., Illinois, Fig. 15e. In this case there is a fairly uniform distribution of ash and sulphur in 96 per cent of the coal. The removal of the heaviest 4 per cent will reduce the ash content by about 2 units and the sulphur content by about one-quarter of a unit.

In Table 23 the flow-sheet is shown for the performance of a pneumatic washer operating on coal from the Kincaid mine, Christian Co., Illinois. At the time these pilot tests were made the coal had a slightly lower sulphur content than that of the samples obtained for the laboratory tests reported here. The results, however, are in good agreement with those predicted by the float-and-sink data for the particular point of cleaning selected.

While the data and results obtained in this phase of the investigation are somewhat inconclusive, it is felt that their presentation here is warranted because of the importance of the subject. The relationship between the fusing-point of coal ash as determined in the laboratory, and slagging and dust deposition in boilers and economizers, has been difficult to establish definitely. An explanation of the discrepancies sometimes found may lie in the failure to realize the difference between the agglomerating, or cohering, temperature of solid particles and the fusing temperature. If the observations of Tammann and Sworykin* on pure substances are true for mixtures of oxides and silicates the agglomeration of particles of ash containing oxides may be expected at temperatures several hundred degrees below the actual fusing point. Besides the distribution of the ash in the coal and the agglomeration temperature, the slagging of boiler tubes is affected by the design and operation of the furnace† to such an extent that any characteristic of the coal may be overshadowed in trying to determine the cause of this trouble.

The conclusions reached in this phase of the investigation may be summarized as follows:

(1) Coals containing a large portion of their ash and sulphur as finely disseminated particles in the bony portion are more apt to produce slagging and dust deposition than coals having the ash largely segregated.

(2) The removal of approximately one-quarter of the ash and

*See footnote p. 54.

†A. G. Christie, "Boiler Furnaces for Bituminous Coals," Proc. Second International Conference on Bituminous Coal, vol. 2, p. 319, Carnegie Inst. of Technology, Pittsburgh, 1928.

TABLE 23

FLOW SHEET OF PNEUMATIC WASHER OPERATING ON ILLINOIS NO. 6 COAL FROM KINCAID MINE, CHRISTIAN COUNTY, ILLINOIS

Size in.	Weight		Raw		Cleaned			Reject			
										Weight	
	lb.	per cent	Ash per cent	S per cent	Ash per cent	S per cent	Weight lb.	Ash per cent	S per cent	lb.	per cent
2 x 1	1733	6.94	15.40	4.97	10.66	3.84	1557	54.08	12.73	174	10.0
1 x ½	7551	30.28	12.80	4.87	10.63	3.71	7021	57.22	15.62	530	7.0
½ x ¼	5587	22.40	14.21	4.44	10.03	3.55	5179	61.33	14.94	408	7.0
¼ x ⅛	3860	15.48	13.14	4.03	10.14	3.70	3624	58.59	10.00	236	6.1
⅛ x 1/16	2000	8.02	13.17	4.20	10.36	3.48	1884	64.32	14.07	116	5.8
<1/16	4209	16.88	17.19	4.90	← Not treated →						
Total	24940	100.00	14.48	4.51	.....	.....	.....	.....	.....	1464	5.87

sulphur in coal can usually be accomplished by the ordinary processes of washing.

29. *Effect of Coal Carbonization on Nature of Stack Gases.*—Some steps have recently been taken in this country and in Europe toward the utilization of various methods for coal carbonization in connection with steam generation, the object being to burn the coke under the boiler and to obtain the gases, tar, and other by-products for outside consumption. While no work on this problem was included in the investigation, it is of interest to observe the effect such treatment will have on the character of the combustion gases.

Ordinarily in the coking of coal some sulphur is given off in the form of hydrogen sulphide and carbon disulphide, thiophene and other compounds. The percentage of sulphur that remains in the coke, however, usually is nearly the same as that in the original coal due to the fact that a loss in weight as well as a loss in sulphur has occurred.

A. R. Powell* has studied the primary reactions of coal sulphur during carbonization and has found that for a large variety of coals the following five sulphur reactions take place:

(1) Complete decomposition of the pyrite to form pyrrhotite and hydrogen sulphide; this reaction begins at 300 deg. C., reaches a maximum between 400 and 500 deg., and is complete at 600 deg.; (2) reduction of sulphate to sulphide, complete at 600 deg.; (3) decomposition of one-fourth to one-third of the organic sulphur to form hydrogen sulphide, mostly below 500 deg.; (4) decomposition of a small part of the organic sulphur to form volatile organic sulphur compounds, most of which find their way into the tar, at the lower temperatures of the coking process; (5) disappearance of a portion of the pyrite, the sulphur appearing in combination with the carbon, at 500 deg. C. or higher.

These results were all based on laboratory experiments performed on small quantities of coal in such a manner that there were no effects produced by the passage of the volatile matter through the coking mass from another portion of the charge. Such secondary effects would be brought about by the presence of hydrogen, and would result in a lowering of the temperature at which the pyrite decomposes, and in a decomposition of the organic sulphur, or carbon-sulphur combinations, to form hydrogen sulphide.

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*A. R. Powell, "A Study of the Reactions of Coal Sulphur in the Coking Process," Ind. Eng. Chem., vol. 12, p. 1069, 1920.

Powell* later made extensive tests on various methods for eliminating sulphur from coke, and showed that of these the steam treatment, or intermittent steam and vacuum, is probably the most efficient. From 20 to 25 per cent of the sulphur in the coke may be removed by this method. The greater part of the sulphur removal takes place at temperatures below 500 deg., and in the first hour of treatment. The sulphate sulphur content remains approximately constant until a temperature of approximately 800 deg. is attained, where it is almost entirely eliminated.

A study of the formation of organic sulphur compounds has also been made recently by Huff and Holtz.† They found evidence that dissociation of hydrogen sulphide on the coke takes place at high temperatures with the resulting formation of carbon-sulphur complexes. The formation of carbon disulphide and other organic sulphur compounds takes place in these complexes. Conditions which favor the fixation of high local-sulphur concentrations, such as sudden heating with diminished diffusion, and reduction of exposed surfaces, together with the rapid removal of the carbon disulphide formed, favor the presence of carbon disulphide in the gas.

It is probable, therefore, that as a result of carbonization, flue gases of only slightly lower sulphur dioxide and sulphur trioxide content could be obtained. The greatest benefit, however, would probably be manifest in the character of the fly ash. It is probable that scale formation on both boiler and economizer tubes would be decreased, and the scale itself would be of an entirely different composition.

IV. Laboratory Study of Corrosion by Flue Gases

30. *Introductory.*—Of the several conditions that appear to be prevalent in flue gases that may cause corrosion any one may act as the controlling factor in the corrosion process. While it has usually been assumed that the condensation of sulphuric acid at temperatures below the dew-point is the sole cause of the corrosion, this could not be accepted as final until the effects of the other conditions had been definitely ascertained. In order to do this it was necessary to establish under what conditions the several factors have the maximum rate of corrosion. The deterioration may be caused by any one, or by

*A. R. Powell and J. H. Thompson, "A Study of Desulphurization of Coke by Steam," Bul. 7, Coal Mining Investigations, Carnegie Inst., 1923.

†Wilbert J. Huff and John C. Holtz, Ind. Eng. Chem., vol. 19, p. 1268, 1927; vol. 22, p. 639, 1930. Work of other investigators is cited in these articles.

any combination of the following: (a) sulphuric acid vapor, (b) condensed sulphuric acid, (c) sulphate scale, (d) moisture, (e) sulphur dioxide, (f) carbon dioxide. There is little probability that the last enters into the corrosion, because it is prevalent in all flue gases. In order to decide what combinations of these items control the rate of corrosion several accelerated tests were carried out in the laboratory.

31. *Principle of Accelerated Test.*—In making an accelerated test on corrosion some care must be taken to establish the conditions in which the item in question is known to be the one which controls the corrosion. Speller* points out that there has been a tendency to generalize conclusions without a sufficiently clear knowledge of the mechanism of corrosion, the factors involved, or the relative controlling influence of these factors. "To design a rational system of corrosion tests for specific purposes," he states, "it is very desirable to have a good working theory of the corrosion process. The greatest principal need, however, is a better understanding of the factors involved in order to properly weigh and balance them in the testing method . . . . Under certain conditions accelerated corrosion tests are permissible when they include all the important factors and conditions found in service and these factors bear the same relation to one another as they do in service, viz., the controlling factors must still control and the unimportant factors remain relatively unimportant."

In order to determine which of the factors enumerated are the most important, tests were made on the corrosion of iron in the presence of several individual conditions and combination of conditions such as would exist in the flue gases. To this end the following series of experiments were made on the rate of corrosion of iron: (1) corrosion by sulphuric acid vapor at relatively high temperatures but below the dew-point, (2) corrosion by concentrated sulphuric acid at high temperatures, (3) corrosion by the sulphate scale at high temperatures, (4) corrosion by the sulphate scale in the presence of moist air at high temperatures, and (5) corrosion by aerated saturated solutions of ferric sulphate in sulphuric acid. A brief description of these tests and their results follows.

32. *Preliminary Corrosion Tests.*—Specimens of soft iron were surrounded by an atmosphere containing sulphuric acid vapor, water vapor, and air at 200 deg. F. The conditions were established by evaporating sulphuric acid and passing the vapors into a closed cabinet

*F. N. Speller, "Corrosion—Causes and Prevention," p. 199, McGraw-Hill Book Company, New York, 1926.

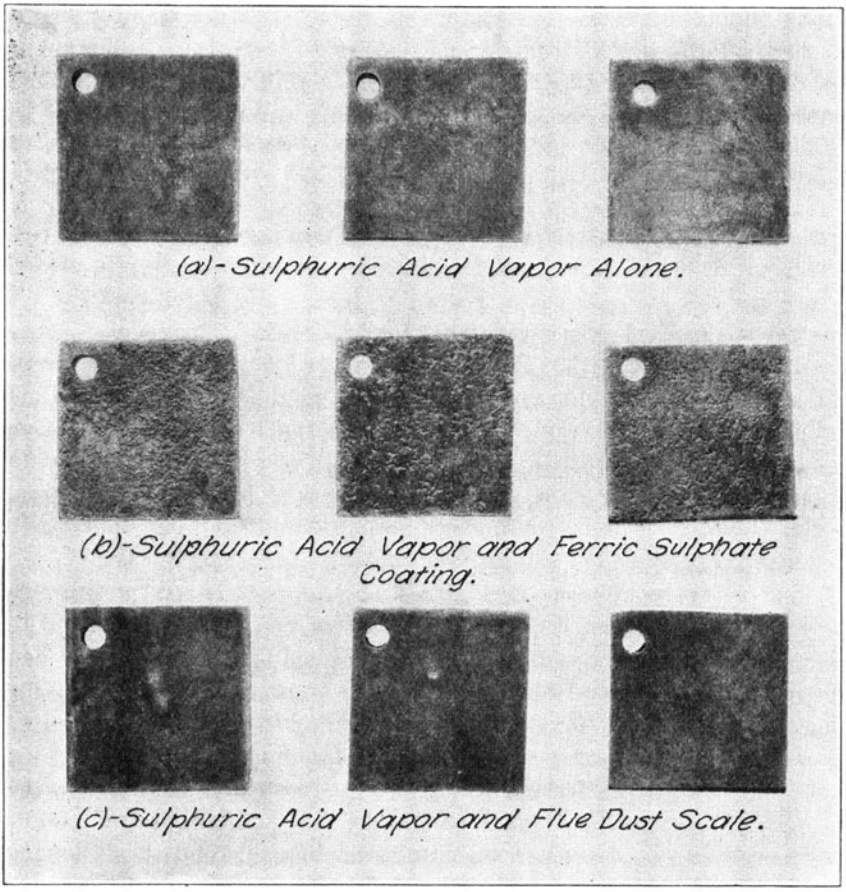

FIG. 16. CORROSION OF PURE IRON AT 200 DEG. F. BY ACID VAPOR

which was maintained at the constant temperature. Although the actual concentration of the acid vapor was small, it was sufficient to cause the formation of a fog even at the temperature of the gases. Droplets of the condensed acid existed on the surface of the metal throughout the test. The corrosion caused by the condensed acid alone was very slight, the penetration amounting to 0.0045 in. per year. Figure 16a shows some of the specimens after two weeks of exposure to the gases. The accelerating effect on the corrosion caused by the presence of solid ferric salts is illustrated by the more severe corrosion shown in Fig. 16b and 16c. The former shows the effect of pure ferric sulphate, and the latter that due to the ferric sulphate in

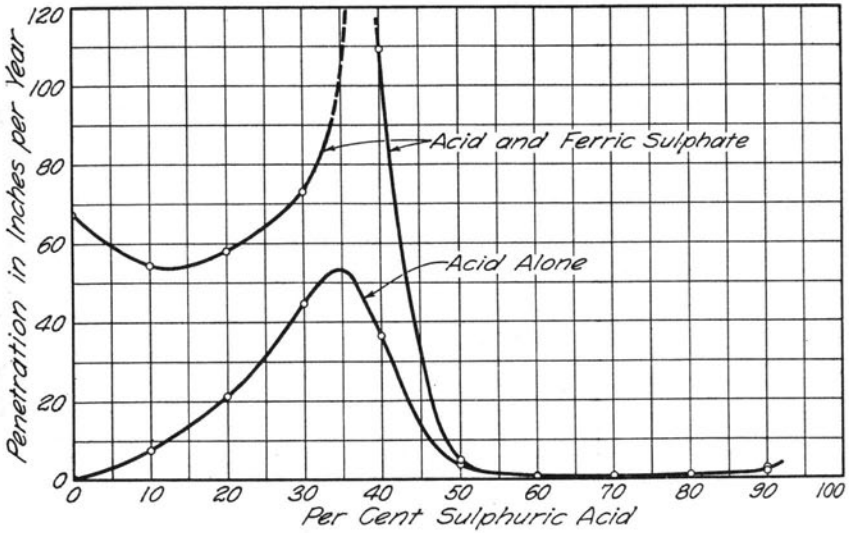

FIG. 17. CORROSION OF PURE IRON AT 200 DEG. F. BY ACID SOLUTIONS

flue dust. The rates of penetration in these cases were 0.0217 and 0.0050 in. per year, respectively. All specimens were surrounded for two weeks by the gases containing sulphuric acid vapor at a temperature below the dew-point.

For comparison, the rate of corrosion of iron by sulphuric acid solutions was then measured. In dilute solution the acid acts like other strong acids and attacks iron rapidly with the evolution of hydrogen. As the concentration of acid increases the rate of attack first increases and then decreases until at a concentration of about 50 per cent the attack is very slow. It has been assumed that passivity of the metal due to some insoluble coating hinders the rate of attack in the more concentrated solutions. The presence of oxygen increases the rate of attack in all cases. The same result is produced by raising the temperature. Since the concentration of acid existing on the metal surface in the preheaters and economizers varies between 50 and 90 per cent according to the temperature of the metal surface, the attack by the acid is usually slow. If for some reason, however, water is added to the acid, such as by condensation on cooling, or by washing, the rate of attack is greatly increased. Figure 17, lower curve, shows the rate of penetration into pure iron by sulphuric acid solutions of various concentrations. The solutions were aerated and maintained at a temperature of approximately 200 deg. F.

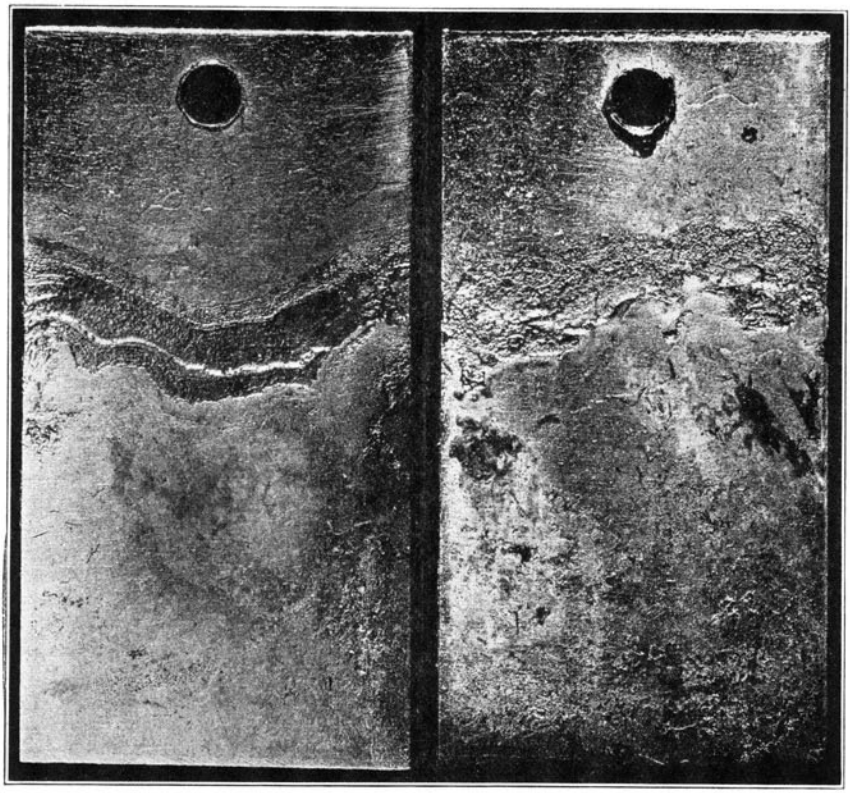

FIG. 18. CORROSION BY FERRIC SULPHATE IN PRESENCE OF MOIST AIR AT 200 DEG. F.

As a third experiment specimens of iron were coated with a sulphate deposit and maintained at a temperature of 200 deg. F. in the air for several hours. Although tarnishing could be noticed, practically no loss of weight was shown.

The rate of attack of the sulphate deposit on iron in the presence of moisture was determined next by coating small bars with this deposit and passing air saturated with moisture at 140 deg. F. over the bars. While the results were not entirely reproducible, corrosion always took place, and was manifested by a pitting under the portions of the scale that adhered to the metal. Apparently the corrosion was most severe when the gas could come in contact with the metal and the scale at the same point. If the scale was too compact the gas could not pass through to the metal and no attack took place. On the other hand, if the scale was so loose that good contact was not

made with the metal, corrosion only took place at the points where it touched the metal.

Experiments on the rate of attack on iron by pure ferric sulphate in the presence of moist air were then carried out. These were made by coating specimens with a paste of the sulphate and passing a mixture of steam and air around them at a temperature of 200 deg. The rate of attack was extremely rapid and did not decrease after twenty-one days; during this time the entire specimen was consumed. Figure 18 shows some of the specimens after two days of such treatment.

Corrosion by pure ferrous sulphate under similar conditions was much less than that by ferric sulphate. Apparently the attack was limited to the amount of ferric sulphate formed by oxidation of the ferrous sulphate.

Two possibilities exist for the explanation of the attack by ferric sulphate, viz., the hydrolysis of the sulphate to form sulphuric acid, and the oxidizing action of ferric ions on the metal. An attempt to decide which of these was the cause of the corrosion was made by determining the action of aluminum sulphate on iron. Under similar conditions this salt also is highly hydrolyzed but does not possess the oxidizing property of ferric sulphate. The attack by aluminum sulphate was negligible under these conditions.

Finally, the effect of the presence of ferric sulphate on the rate of attack of sulphuric acid solutions of various concentrations was studied. Pure iron specimens were suspended from glass hooks into solutions of sulphuric acid saturated with ferric sulphate. The temperature was maintained at 200 deg. F. The solutions were aerated with perforated glass tubes. The results of these corrosion tests are shown in Fig. 17, upper curve. At concentrations of acid below 50 per cent the rate of attack was greatly increased by the presence of the ferric sulphate. Above this concentration, while the loss was always greater in the presence of the ferric sulphate, the effect was somewhat obscured by the passivity of the metal.

These results agree with those obtained by Hall and Teague* on the corrosion of metals and alloys in acid mine water. These authors studied the rate of attack of various dilute solutions of acids, bases, and salts in the presence and absence of ferric sulphate on copper, tin, and zinc, and on certain alloys composed of these metals and of nickel, chromium, iron, lead, and silver. They found that the rates

*R. E. Hall and W. W. Teague, "The Effect of Acidity and Oxidation Capacity on Corrosion of Metals and Alloys in Acid Mine Water." Carnegie Inst., Coal Mining Invest. Bul. 15, 1924.

of attack of all solutions were greatly increased by the presence of ferric sulphate. Aluminum sulphate did not increase the rate of attack, although the hydrolysis of the salt is similar to that of ferric sulphate. Likewise, chromium sulphate, which is also highly hydrolyzed and possesses a large oxidizing potential, was not effective in increasing the rate of corrosion. Apparently the ability of the chromic ions to render the metal temporarily passive prevented the manifestation of any oxidizing property of this substance. Stannic ions possess oxidizing properties similar to ferric ions and were found to increase the rate of corrosion correspondingly.

It is interesting to note that the attack of acid solutions containing ferric sulphate on copper and on copper alloys was greatly increased due to this oxidizing property. While the use of copper steel and of the brasses and bronzes has proved advantageous in the presence of acids alone, they cannot be recommended when oxidizing agents such as ferric or stannic ions are present. This explains many of the contrary statements as to the durability of copper steel under various conditions.

Hall and Teague write, "While in the case of zinc at the higher acidities the replacement of hydrogen ion may be the predominating mechanism of corrosion and the reduction of ferric ion secondary, the latter was always a major mechanism for the solution of tin and copper." They conclude that the results admit of no doubt as to the major factor of corrosion in an acid mine water. In those alloys in which passivity or film formation is not a factor the acid concentration exercises a minor function and the potential of the cell

metal, metal ion, electrolyte, Fe^{++}, Fe^{+++}

governs the reaction at the metal surface. Although these authors examined only a few alloys containing iron, and their conditions were limited to the relatively low concentrations of ferric salts that are encountered in certain mine waters, their conclusions undoubtedly apply equally as well to the attack on steel by saturated solutions of ferric salts.

33. *Accelerated Corrosion Tests.*—The results of the corrosion experiments outlined leave little doubt that the saturated acidic solution of ferric salts formed at temperatures below the dew-point is responsible for the corrosion in economizers and preheaters. An accelerated corrosion test based on this controlling factor should indicate the relative resistance of metals to the condition encountered in flue gases. Such a test is warranted because of the length of time and expense required by a long-time service test.

The sulphuric acid concentrations selected for the tests were 36 and 50 per cent. These represent, respectively, the concentration most corrosive toward iron and a concentration at which marked passivity is manifested. The stronger acid probably more nearly approximates the service conditions. These solutions were saturated with ferric sulphate and maintained at 200 deg. F. on a steam bath. A current of air was passed through the solution during the tests. To prevent loss of water and a concentrating of the acid due to the high temperature a reflux condenser was used.

The metals were cut into specimens 1 in. square and ⅛ in. thick. The area exposed was 2½ sq. in. The specimens were drilled and stamped with identifying numbers. They were suspended into the solution on glass rods. All tests were run in duplicate, and a different solution was used for each specimen. The tests were run for a period of one hour; after this the samples were removed, washed in water, dried, and weighed. They were then returned to the same solution and the tests continued for two more hours. For comparison, the rates of corrosion of all the metals in the same concentrations of acid but without the ferric sulphate were measured.

The results of these tests are shown in Table 24.* The rates of corrosion are expressed in milligrams lost per square centimeter per hour. These may be converted to penetration in inches per year by multiplying by the factor $\frac{0.125}{\text{density in lb. per cu. in.}}$. The appearance of some of the more important alloys after the 3-hour attack is shown in Fig. 19. The blank spaces in the pictures indicate that the corresponding specimens were completely dissolved.

The practical results of these tests were summarized in Chapter III. The data are also interesting from a theoretical standpoint because of the effects of oxidizing capacity on corrosion.

34. *Effects of Oxidizing Capacity of Ferric Ions on Development of Passivity.*—The differences in the rate of corrosion during the first hour and that during the second and third hours are due in general to the development of passivity of the metal surface. It is to be noticed that the decrease is greater in the presence of ferric sulphate than in the pure acid. Also the presence of chromium in the alloy shows little effect on the rate of corrosion by pure acid during the first hour. In the later period the decrease in corrosion is greater when chromium is present. The almost immediate attainment of passivity by the chromium alloys in the presence of ferric sulphate

*The author is indebted to Mr. N. A. Young for the experimental work on the accelerated tests.

TABLE 24

ACCELERATED CORROSION RATES OF METALS AND ALLOYS

Reference No.	Approximate Chemical Composition per cent (When the percentages shown do not total 100 the difference may be considered as iron.)	Corrosion Loss, Milligrams per Square Centimeter per Hour							
		H_2SO_4 at 200 deg. F.				H_2SO_4 Saturated with Ferric Sulphate at 200 deg. F.			
		Aerated—36 per cent acid		Aerated—50 per cent acid		Aerated—36 per cent acid		Aerated—50 per cent acid	
		1st hr.	2nd and 3rd hr.	1st hr.	2nd and 3rd hr.	1st hr.	2nd and 3rd hr.	1st hr.	2nd and 3rd hr.
1	Pure Fe	75.0	86.2	59.2	0.3	211.1	132.2	66.4	4.2
2	Cu 0.45; Mo 0.07; C 0.63	25.4	14.6	30.0	1.3	84.4	61.2	21.5	11.7
3a	Cr 28; Ni 2	78.9	136.4	141.0	125.2	0.0	0.0	0.0	0.1
3b	Cr 28; Ni 2	892.2	.....	625.3	115.1	0.5	0.0	0.8	0.0
4	Cr 28.3; Ni 0.5	318.7	304.7	728.0	20.5	0.1	0.0	0.2	0.2
5	Cr 30	423.3	263.2	551.5	....	0.4	0.1	0.3	0.2
6	Cr 12.4; Ni 0.27; Mn 0.5	234.5	12.1	418.9	10.4	388.0	0.3	202.0	34.0
7a		106.0	43.4	9.7	112.8	0.6	0.0	0.1	0.0
7b		34.6	0.1	67.5	108.0	0.4	0.1	0.1	0.0
7c	Cr 18; Ni 8; Si 0.7; C 0.15	66.4	0.1	20.9	0.1	0.4	0.0	0.4	0.0
7d		173.4	180.2	231.2	210.8	0.1	0.0	0.1	0.0
7e		44.0	35.6	111.4	88.8	0.2	0.0	0.2	0.2
8	Cr 20; Ni 7; Si 1.4; W 3.8; C 0.34	132.0	161.2	234.5	102.5	0.1	0.0	0.0	0.0
9	Cr 15; Ni 25; C 0.3	26.4	20.6	31.0	24.8	0.2	0.0	0.0	0.0
10	Cr 20; Ni 20	5.7	11.4	5.3	4.0	0.2	0.2	0.4	0.1
11	Cr 15; Ni 61; Mn 2; Si 0.1; C 0.15	0.8	0.7	2.6	2.3	0.9	0.0	14.2	0.0
12a	Cr 20; Ni 68 rolled	1.3	0.5	1.6	4.2	3.8	4.7	11.6	12.1
12b	Cr 20; Ni 68 cast	0.2	23.6	1.6	2.1	53.2	36.7	12.5	10.1
13a	Cr 21; Ni 12; C 0.25	91.6	270.6	91.3	110.1	0.2	0.0	0.1	0.1
13b		22.7	21.4	31.7	14.1	0.2	0.0	0.2	0.0
14	Cr 28; Ni 25	61.3	47.4	730.3	45.7	0.0	0.0	0.0	0.0
15	Cr 12; Ni 60; W 3.5; Mn 1; Si 0.35	0.6	3.5	1.1	5.5	57.1	38.8	11.5	14.6

TABLE 24 (CONCLUDED)

Reference No.	Approximate Chemical Composition per cent (When the percentages shown do not total 100 the difference may be considered as iron.)	Corrosion Loss, Milligrams per Square Centimeter per Hour							
		H_2SO_4 at 200 deg. F.				H_2SO_4 Saturated with Ferric Sulphate at 200 deg. F.			
		Aerated—36 per cent acid		Aerated—50 per cent acid		Aerated—36 per cent acid		Aerated—50 per cent acid	
		1st hr.	2nd and 3rd hr.	1st hr.	2nd and 3rd hr.	1st hr.	2nd and 3rd hr.	1st hr.	2nd and 3rd hr.
16	Cr 11; Ni 36; Mn 1.5; Si 0.2	0.6	1.0	2.3	0.8	0.2	46.3	1.5	6.5
17	Cr 12; Ni 35; Si 5	0.4	0.1	0.3	0.1	2.2	0.5	8.6	0.8
18	Cr 7; Ni 20; Mn 0.5	1.2	0.8	1.5	0.3	38.5	1.5	117.9	9.5
19	Ni 30	0.7	10.1	15.6	1.8	72.8	5.5	19.6	3.0
20	Ni 64; Cu 24; Al 2	1.0	0.9	0.7	3.4	26.4	48.0	9.0	6.0
21	Ni 60; Mo 20	0.6	1.9	0.6	0.2	31.6	7.5	9.7	9.7
22	Pb 99.4	1.3	0.2	1.2	0.2	0.8	0.1	0.5	0.1
23	Pb 93; Sb 7	0.7	0.1	0.6	0.1	0.7	0.0	0.6	0.1
24	Pure Cu	0.4	0.5	0.2	0.2	40.0	44.3	13.6	13.3
25	Cu 88.5; Ni 5; Sn 5; Si 1.5	8.0	0.2	1.2	1.0	30.6	26.1	15.1	9.1
26	Cu 64.4; Ni 29.7; Zn 5.3; Mn 0.6	0.3	0.5	0.2	0.3	30.8	30.1	6.9	12.7
27	Cu 73.6; Ni 19.7; Zn 6.3; Mn 0.4	0.2	0.3	0.3	0.3	32.3	24.5	10.9	11.2
28	Cu 85.3; Zn 14.7	0.2	0.5	0.3	0.4	87.4	42.5	14.5	13.9
29	Cu 70.4; Zn 28.4; Sn 1.2	0.5	0.4	0.4	0.3	33.1	21.7	17.3	12.2
30	Cu 61.0; Zn 38.9; Pb 0.1	0.4	0.4	0.2	0.1	41.1	8.2	6.4	2.1
31	Cu 98.2; Sn 1.2	0.3	0.5	0.3	0.5	46.0	35.4	10.3	12.1
32	Cu 97.2; Sn 2.1; Si 0.6	0.4	0.4	0.4	0.5	....	45.1	13.9	11.7
33	Cu 96.0; Si 3.0; Mn 0.9	0.0	0.7	0.5	0.3	15.5	20.3	97.8	9.6
34	Cu 98.8; Cd 1.1	0.3	0.7	0.2	0.3	26.8	6.2	14.3	10.5
35	Cu 96.1; Sn 1.9; Al 2.0	0.4	0.4	0.2	0.3	39.7	38.9	53.8	11.9
36	Cadmium plate on Fe	← No protection →							
37	Phosphate coating (chemical)	← No protection →							
38	Phosphate coating (electrolytic)	← No protection →							

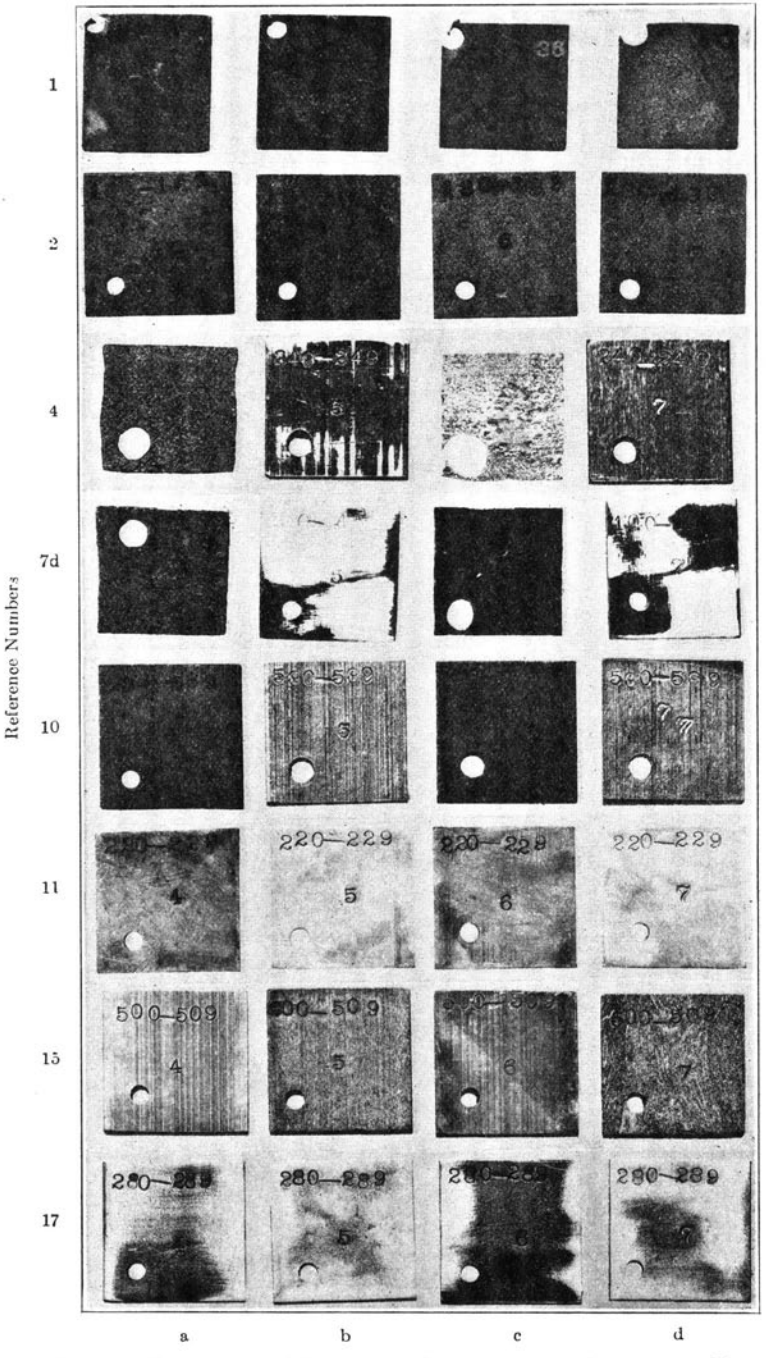

FIG. 19. CORROSION OF METALS AND ALLOYS DURING ACCELERATED TESTS

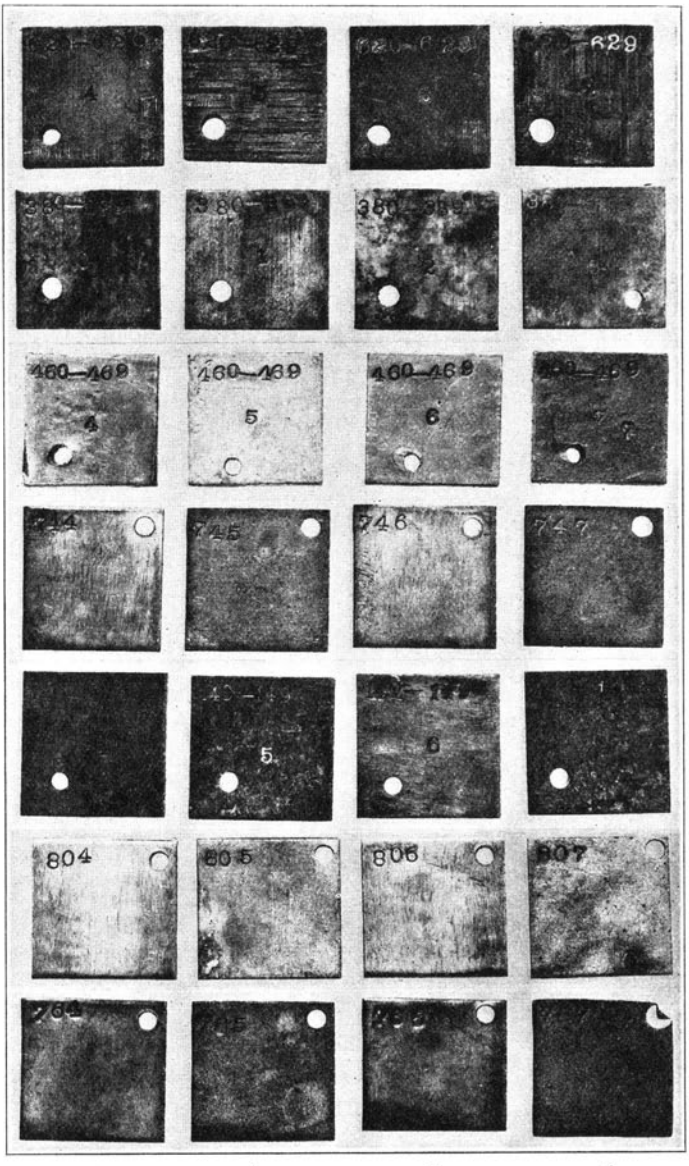

FIG. 19 (CONTINUED). CORROSION OF METALS AND ALLOYS DURING ACCELERATED TESTS

(a) Aerated 50 per cent sulphuric acid at 200 deg. F.
(b) Same as (a)—saturated with ferric sulphate.
(c) Aerated 36 per cent sulphuric acid at 200 deg. F.
(d) Same as (c)—saturated with ferric sulphate.

See Table 24 for description.

has already been mentioned. These facts lead to some interesting conclusions concerning the development of passivity.

The phenomenon of passivity has recently been studied intensively by W. J. Müller.* In his work a small electrical current was used to produce the corrosion of many types of metals. The essential feature of Müller's views on passivity is that the phenomenon does not set in until the liquid next to the anode becomes saturated with some compound of the anodic metal. Thus the attainment of passivity requires a definite time interval. With iron and nickel these deposits have been identified as hydrated sulphates. Müller also distinguishes between two stages of passivity: (a) a primary, or surface passivity due to the accumulation of the insoluble compound, and (b) secondary, or chemical passivity due to changes in the atoms on the surface of the metal brought about by the high current density after primary passivity is attained. In accordance with these views any environment that increases the rate at which a metal passes into solution and does not increase the solubility of the corrosion product should decrease the time required for the attainment of passivity. Ferric ions exert such an action. In the presence of ferric sulphate the corrosion of iron falls off more rapidly than in pure acid. Chromium steels should be as active as or even more active than pure iron at the instant they are placed in the solution. In pure acid they become passive somewhat faster than iron. In ferric sulphate—acid solutions the development of passivity is very rapid because of the instantaneously high initial rate of corrosion and the characteristic property of passivity shown by chromium.

35. *Corrosion Tests on Paints.*—These tests were made in an atmosphere of flue gases containing about 0.3 per cent sulphur dioxide and 0.01-0.02 per cent sulphur trioxide. The gases were obtained by burning city gas with a constant ratio of air in a specially designed burner. The tests were carried on in a large double-wall thermostat maintained at 200 deg. F. The CO_2 content of the gas was approximately 9 per cent, and the moisture 10.5 per cent by volume. The panels were hung in the gases and duplicates were imbedded in ferric sulphate in the thermostat. The test was continued for 90 days.

The results of the tests are shown in Table 25 and in Fig. 20. Unfortunately the manufacturers of the paints did not specify their nature, but it was evident that many of them were of asphaltic nature

*W. J. Müller, Monatshefte für Chemie, vol. 48, pp. 303, 711, 1927; vol. 49, p. 47, 1928; vol. 50, p. 289, 1928; vol. 51, p. 1025, 1929; vol. 52, p. 289, 1929; Z. phys. Chem., vol. 141A, p. 343, 1929; Z. Elektrochem., vol. 34, pp. 571, 858, 1928; vol. 35, p. 656, 1929; cf. also discussion by U. R. Evans, Chem. and Ind., vol. 49, pp. 66T, 92T, 1930.

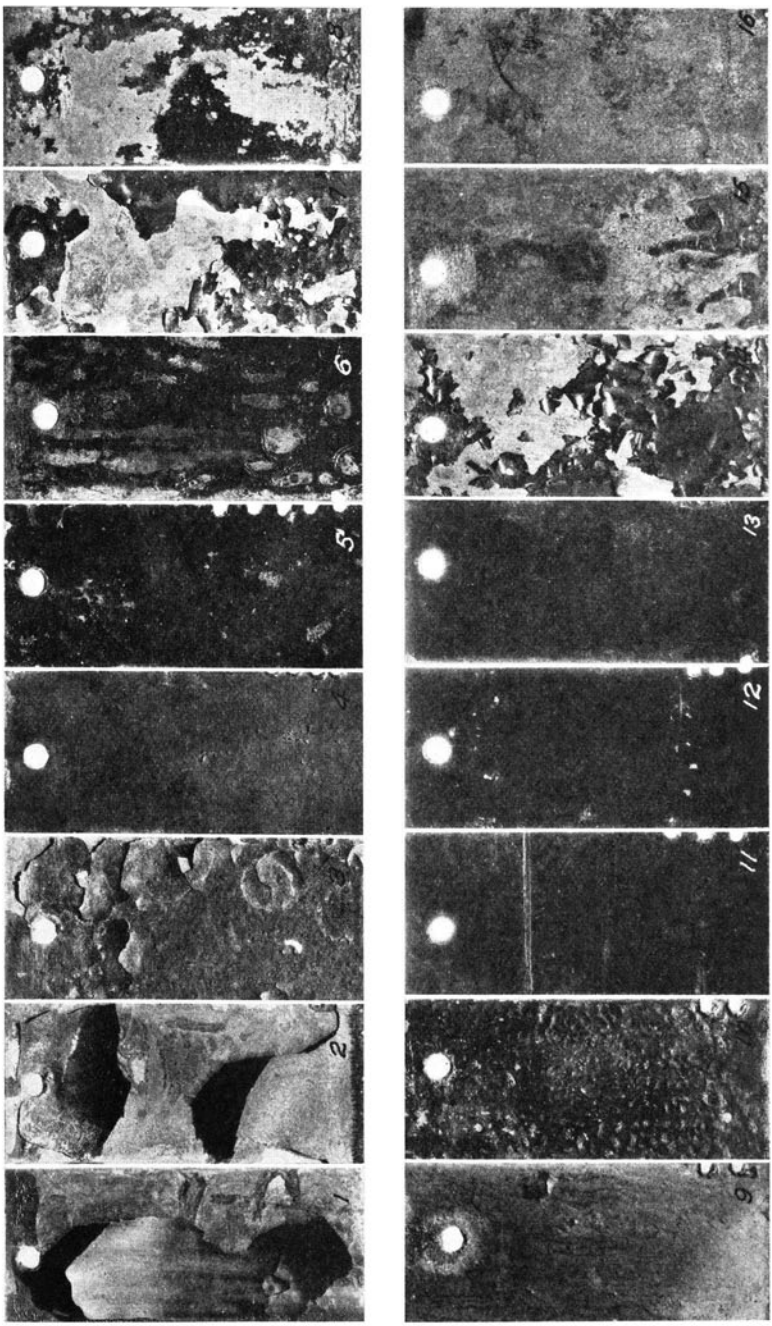

FIG. 20. EFFECT OF FLUE GASES ON PAINTS
See Table 25 for description.

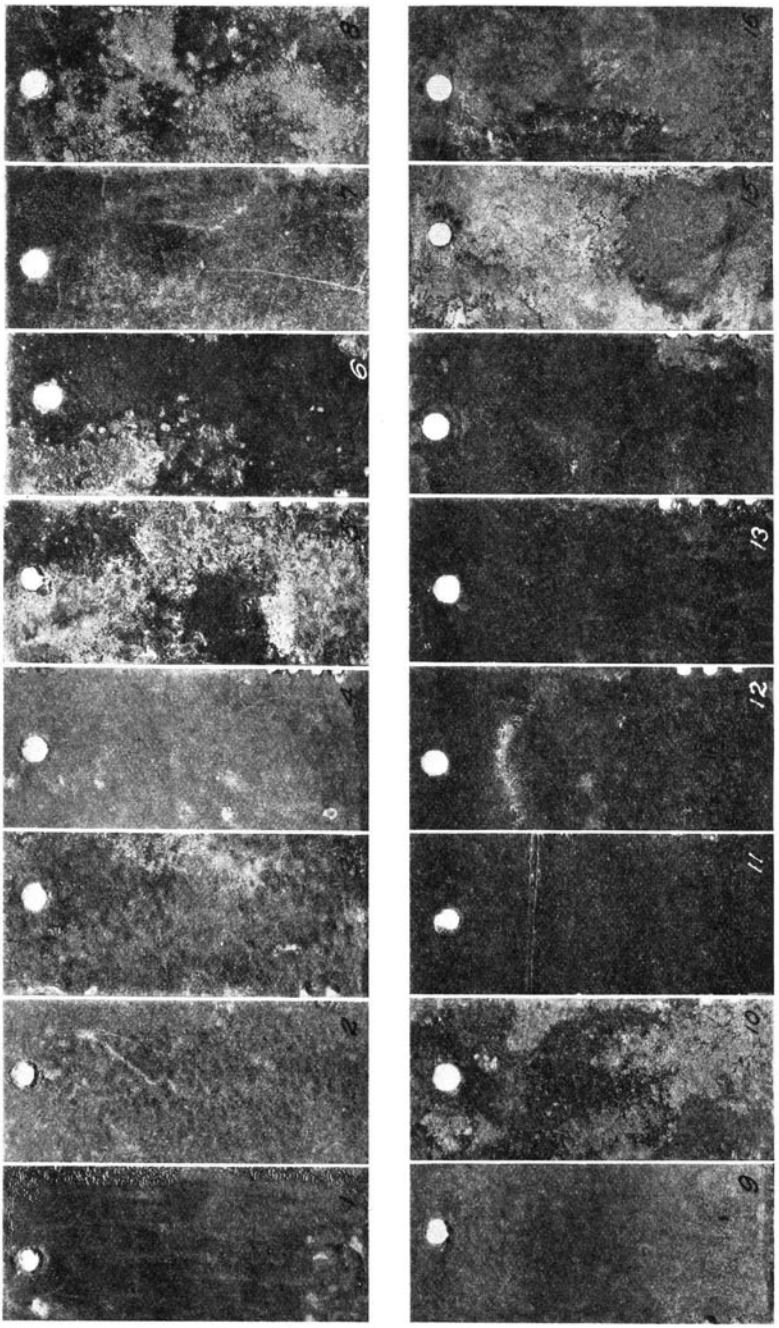

FIG. 21. EFFECT OF FERRIC SULPHATE ON PAINTS

See Table 25 for description.

TABLE 25
EFFECT OF FURNACE GASES AND FERRIC SULPHATE ON PAINTS AT 200 DEG. F., 90 DAYS

Reference No.	Description	Suspended in Gases	Imbedded in Sulphate in Gases
1	Silica-graphite-black	Peeled badly	Discolored and roughened; did not peel
2	Silica-graphite-natural	Peeled badly	Discolored and etched
3	Silica-graphite-heat resisting	Peeled badly	Blistered and peeled
4	Gray paint	Discolored and peeled on edges only	Discolored and attacked slightly at points
5	Tar-petroleum mixture	Slightly blistered and peeled	Destroyed
6	Coal-tar mixture	Badly attacked	Badly attacked
7	Tar-petroleum mixture	Blistered and peeled	Blistered and peeled
8	Asphaltic	Peeled	Badly blistered
9	Red paint	Discolored and peeled	Blistered and discolored
10	Coal tar mixture	Blistered and peeled	Blistered and peeled
11	Resinoid—2 coats baked at 275 deg. F.	Very good—no deterioration	Very good—no deterioration
12	Resinoid—2 coats baked at 275 deg. F.	Flaked at few points	Very good
13	Resinoid—2 coats baked at 570 deg. F.	Flaked at edges	Flaked at edges
14	Resinoid enamel—2 coats air dried	Peeled badly	Peeled at few points
15	Resinoid lacquer—2 coats baked at 400 deg. F.	Coating dissolved	Coating dissolved
16	Resinoid lacquer—2 coats baked at 400 deg. F.	Coating dissolved	Coating dissolved

with graphite and silica as fillers. These were the only paints recommended as being able to withstand high temperatures in the presence of the gases. The tests showed that these also were attacked, probably by penetration of the acid gases to the metal beneath. A few of the artificial resinoid types gave promising results.

Appendix A

Comparison of Accuracy of Analytical Methods for Determination of Sulphur Dioxide and Sulphur Trioxide in Boiler Furnace Gases—A New Method of Analysis

The conflicting statements found in the literature* concerning the extent of oxidation of SO_2 in flue gases indicates the varying degrees of accuracy of the methods used for the separation of the dioxide and trioxide. The importance of arriving at some definite conclusion on this subject warranted an extended investigation of these methods. In the end a new analytical method was developed, which could be easily carried out in a power plant, and which gave accurate results.

1. *Requirements of Analytical Method.*—An analytical method for the determination of SO_2 and SO_3 must overcome the following difficulties:

(1) Condensation of sulphuric acid with a resulting decrease in the SO_3 concentration prohibits the storage of the gas before the analysis. (2) The oxidation of SO_2 to SO_3 by the oxygen present in the gases is sufficient to change the ratio of the oxides materially, especially when the gases are passed through water or alkaline solution. (3) The small amount of SO_3 compared with the amount of SO_2 present in flue gases makes the indirect determination of the former from the total sulphur and SO_2 values very inaccurate. (4) To be serviceable in a power plant, the method and apparatus must be simple, accurate, and rapid.

2. *Methods Previously Used.*—The literature contains many references to methods used for the determination of SO_2 and SO_3. The Reich† method is commonly used for the determination of SO_2 gases from sulphur burners. This consists in drawing the gases through a known quantity of standard iodine solution containing a little starch. The percentage of SO_2 is estimated from the amount of gas required to decolorize the starch-iodine solution. Various refinements have been suggested‡ for this method.

*Thüler, "The Behavior of the Sulphur in Coal during Combustion," Tonind. Ztg., vol. 37, p. 1853; cf. Chem. Abstracts, vol. 8, p. 1003.
R. A. Sherman and co-workers, "Refractories Service Conditions," Mech. Engineering, vol. 48, pp. 1115 and 1389, 1926; vol. 49, p. 1085, 1927.
J. F. Barclay, "The Sulphur Problem in Burning Coal," Bureau of Mines Tech. Paper No. 436, 1928.
E. Ardern and R. V. Wheeler, "Treatment of Sulphur Fumes in Connection with the Working of the Proposed Electric Power Station at Battersea," Interim Report, Ministry of Transport, London, 1929.
†See L. M. Dennis and M. L. Nichols, "Gas Analysis," p. 284, MacMillan Co., New York, 1929.
‡Raschig, Z. angew. Chem., vol. 22, p. 1182, 1909.

The usual method for the determination of SO_2 in the air is that devised by the Selby Smoke Commission* in which the gas is absorbed by 0.002 normal solution of iodine containing starch. Standard iodine is then added until the color matches that of a blank determination. Sweeney, Outcault, and Withrow† substituted potassium permanganate for the iodine solution. Ferguson‡ recommended bubbling the sample through an excess of iodine solution, allowing the gas to stand over the iodine, and then titrating the excess with sodium thiosulphate. Lowe§ used a solution of sodium iodide and iodate to absorb the SO_2, and after scrubbing a measured volume of gas, the solution was acidified and titrated with sodium thiosulphate. Thomas and Cross¶ developed an automatic sampling device for use with the Selby Commission's method. This was later adapted to complete automatic determination of SO_2 in air by substituting a slightly acidulated solution of hydrogen peroxide for the iodine, and recording the change in electrical conductivity of the solution due to the formation of sulphuric acid from the SO_2.** Schmidt†† used iodine as an absorbent and varied the concentration for the purpose of getting selective absorption of SO_2 and SO_3.

For the simultaneous determination of SO_2 and SO_3 Lunge‡‡ recommended passing the gases through standard sodium hydroxide solution in the presence of phenolphthalein until the color disappeared. The sulphite was then determined by titration with potassium iodate in acid solution. Ljungh,§§ using the same principle, determined the combined values of the oxides by absorption in sodium hydroxide, and then determined the SO_2 separately by absorption in iodine. Dieckmann¶¶ absorbed the gases in sodium hydroxide and used the two indicators, methyl orange and phenolphthalein, to determine the end-points. Sander*** used sodium hydroxide as an absorbent, aspirating the gas until the methyl orange end-point was reached to determine the combined values of the oxides, and then determined the dioxide by adding mercuric chloride which liberated an amount of hydrochloric acid equivalent to the SO_2. This acid was then titrated with sodium hydroxide.

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*Report of the Selby Smoke Commission. Bureau of Mines Bul. No. 98, 1915; cf. also McKay and Ackerman, Ind. Eng. Chem., vol. 20, p. 538, 1928.

†Sweeney, Outcault, and Withrow, Ind. Eng. Chem., vol. 9, p. 949, 1917.

‡Ferguson, Jour. Am. Chem. Soc., vol. 39, p. 364, 1917.

§Lowe, Jour. Soc. Chem. Ind., vol. 40, p. 163, 1921.

¶Thomas and Cross, Ind. Eng. Chem., vol. 20, p. 645, 1928.

**Thomas and Abersold, Ind. Eng. Chem., Anal. Ed., vol. 1, p. 14, 1929.

††Schmidt, Z. angew. Chem., vol. 39, p. 732, 1926.

‡‡Lunge, Z. angew. Chem., vol. 3, p. 563, 1890; "Technical Methods of Chemical Analysis," Gurney and Jackson, London, vol. 1, p. 299, 1908.

§§Ljungh, Chem. Ztg., vol. 33, p. 143, 1909.

¶¶Dieckmann, Papierfabr., vol. 19, p. 285, 1921; also in Chem. Ztg, vol. 45, p. 885, 1917.

***Sander, Chem. Ztg., vol. 45, pp. 261 and 554, 1921.

Haller* recognized that the oxidation of SO_2 to SO_3 takes place when the gases are passed along with oxygen through a solution of sodium hydroxide, and suggested using glycerine to inhibit this oxidation. The oxidation of sodium sulphite solutions had previously been studied by Titoff† who found that copper salts greatly increase the rate of oxidation. Berl‡ investigated many substances that might be used as an inhibitor, and advocated stannous chloride as the negative catalyst. Ries and Clark§ used this substance as an inhibitor, and absorbed the gases in sodium hydroxide solution. The SO_2 content was then determined by titration with potassium iodate in the presence of carbon tetrachloride, after the solution had been made acidic with strong hydrochloric acid. These authors investigated the accuracy of many of the other methods previously suggested, including those utilizing iodine and permanganate, and found that the results were unsatisfactory. The Reich method itself gave consistently low and erratic results.

Among other methods that have been proposed for the analysis of these gases, Pellet¶ absorbed the trioxide in hydrochloric acid and determined it gravimetrically after precipitation with barium chloride. Richter** collected the SO_3 in condenser tubes and determined it gravimetrically. Dunn†† absorbed the gas in barium chloride solution containing hydrochloric acid, removed the dioxide by boiling, and determined the trioxide gravimetrically. Gille‡‡ collected the trioxide on a plug of cotton. Eckman,§§ in determining the SO_3 present in commercial liquid SO_2, precipitated it as barium sulphate in a slightly acid solution of barium sulphite, and, after filtration, washed the precipitate with oxygen-free distilled water in an atmosphere of oxygen-free nitrogen.

Hawley¶¶ removed the trioxide from smelter gases by filtering the cold gases through a filter paper moistened with water to collect the sulphuric acid fog, and then titrated the acid with standard alkali. This method was also approved by Nestell and Anderson,*** and by Weber.††† The method, modified by substituting an alundum thimble for the filter paper, was investigated for use in furnace gases and ap-

*Haller, Jour. Soc. Chem. Ind., vol. 38, p. 52, 1919.
†Titoff, Z. physik. Chem., vol. 45, p. 641, 1903.
‡Berl, Chem. Ztg., vol. 45, p. 693, 1921.
§Ries and Clark, Ind. Eng. Chem., vol. 18, p. 747, 1926.
¶Pellet, Bul. assoc. chim. suecr. dist., vol. 27, p. 468, 1909.
**Richter, Z. angew. Chem., vol. 26, p. 132, 1913, cf. also Wochbl. Papierfabr., vol. 54, p. 1521, 1923.
††Dunn, Bul. Am. Inst. Min. Eng., vol. 80, p. 2051, 1913.
‡‡Gille, Z. angew. Chem., vol. 39, p. 401, 1926.
§§Eckman, Bureau of Standards Scientific Papers, No. 554, 1927.
¶¶Hawley, Eng. Min. Jour., vol. 94, p. 987, 1912.
***Nestell and Anderson, Ind. Eng. Chem., vol. 8, p. 258, 1916.
†††Weber, Ind. Eng. Chem., vol. 16, p. 1239, 1924.

parently gave good results for gases containing high concentrations of SO_3.* A further discussion of its applicability will be given later.

Saillard and Bregmann† have used a method based on the electrical conductivity of solutions for the analysis of these gases. White‡ used the same principle for a continuous recording apparatus for carbon monoxide and for ammonia, and pointed out its usefulness for SO_2.

Palmer and Weaver§ pointed out the applicability of the thermal conductivity method to the analysis of mixtures of SO_2 and air. Dommer¶ devised an automatic determination of the dioxide in roaster gases based on the buoyancy of the gas. Pozzi-Escot** determined its concentration in air by passing the mixture over iodine pentoxide in a quartz tube. The liberated iodine was condensed and dissolved in chloroform in which the concentration was determined colorimetrically.

The method used for the determination of SO_2 and SO_3 reported by Wheeler and Ardern†† consisted in drawing two samples of gas, one through a solution of sodium hydroxide, and the other through a solution of standard sodium hydroxide containing a small amount of hydrogen peroxide. The difference in the titrations of the two solutions with standard acid to the methyl orange end-point was taken as equal to one-half of the SO_2, while the titration of the latter solution gave the total sulphur present.

The analytical method used in the study of refractories service conditions by Sherman and his co-workers consisted in drawing a sample of the gas through a solution of potassium hydroxide. The solution was later separated into two equal portions. The sulphate present in one portion was determined gravimetrically as barium sulphate. The total sulphur in the other portion was also determined gravimetrically after oxidizing the sulphite to sulphate by means of bromine water.

3. *Analytical Tests.*—A survey of the many methods used for the determination of SO_2 and SO_3 indicates that they fall into two groups, viz., (a) those in which the gases are first absorbed in an aqueous solution and trioxide determined either indirectly from the difference in the SO_2 and total sulphur values, or directly by precipitation with barium chloride, followed by the direct or indirect determination of the

*Taylor and Johnstone, Ind. Eng. Chem., Anal. Ed., vol. 1, p. 197, 1929.
†Saillard and Bregmann, Rev. gen. chim., vol. 20, p. 69, 1918.
‡White, Jour. Am. Chem. Soc., vol. 50, p. 2148. 1928.
§Palmer and Weaver, Bureau of Standards Tech. Papers No. 249, 1924.
¶Dommer, Chem. Ztg., vol. 50, p. 382, 1926.
**Pozzi-Escot, Ann. chim. anal. chim. appl., vol. 6, p. 111, 1924; cf. Chem. Abs., vol. 18, p. 1800, 1924.
††Private communication from Prof. R. V. Wheeler, Sheffield Univ.

TABLE 26
RETENTION OF SULPHURIC ACID VAPOR BY DENSE (RA360) ALUNDUM

No.	H_2SO_4 Taken milligrams	H_2SO_4 Retained by Thimble milligrams	H_2SO_4 Not Evaporated milligrams	H_2SO_4 Lost milligrams	Recovery of Evaporated Acid per cent
1	114.5	107.2	5.3	2.0	98.4
2	121.4	105.5	16.8	...	100.8
3	120.5	119.6	2.1	...	101.0
4	119.6	106.3	8.6	4.7	96.0
5	124.1	109.2	6.1	8.8	92.6
6	43.66	41.66	1.08	0.92	97.8
7	10.99	10.07	0.26	0.66	93.8
8	10.99	9.53	0.72	0.74	92.8
9	10.99	10.14	0.28	0.57	94.7

dioxide; and (b) those in which SO_3 is separated as sulphuric acid fog from the gases by filtration, and then the two sulphur gases determined separately.

The applicability of the latter method to flue gases was tested. The accuracy was determined by the analysis of gas-air mixtures which contained known amounts of SO_2 and SO_3. The former was generated from sodium bisulphite and sulphuric acid and was stored and measured in a mercury-sealed gas burette. A measured volume of the gas was mixed with air and passed through a tube which contained a known amount of standardized sulphuric acid and which was heated electrically to about 450 deg. C. The ratio of the concentration of the sulphur gases in this mixture was about 1:1, a ratio which corresponded to the relative concentrations previously reported by other investigators. The gas-air mixture was drawn through a very fine (RA360) alundum thimble by which the sulphuric acid fog was retained. The SO_2 was then absorbed in a known amount of standard sodium hydroxide containing hydrogen peroxide. The amount of acid retained by the thimble was determined by washing it out with water and titrating with standard base. The SO_2 absorbed in the hydroxide was determined from the amount of hydroxide neutralized. The results of these tests are shown in Table 26, items Nos. 1-5. For the amounts of SO_3 used the accuracy justified the application of the method to flue gases.

In the actual use of the method, however, two difficulties were encountered. First, the porosity of the alundum thimble required to remove the fog was so extremely fine that it was impossible to prevent it becoming clogged by the small particles of dust carried by the gas. The increased load on the pump used for drawing the gases caused

TABLE 27
ACTION OF SULPHURIC ACID ON ALUNDUM AND SINTERED GLASS

No.	H_2SO_4 Taken milligrams	Dilution Water cu. cm.	Recovery		
			milligrams	per cent	
1	10.42	100	9.31	89.3	Alundum Medium Porosity
2	10.42	100	9.80	94.0	
3	10.42	100	9.61	92.2	
4	10.42	100	9.35	89.7	
5	10.42	100	10.07	96.5*	
6	10.42	100	9.85	94.4	
7	10.42	100	9.34	89.5†	
8	19.88	100	19.87	100.0	Sintered Glass Medium Porosity
9	19.88	100	19.88	100.0	

*Thimble soaked for 1 week in acid and washed until acid-free.
†Acid stood in contact with thimble for 30 minutes.

by this resistance made the determinations very slow. Secondly, the values obtained by this method were variable and much lower than any values previously reported. The efficiency of the removal of sulphuric acid fog by the alundum thimble was then tested using much smaller amounts of the acid in the evaporator. The results of these tests are shown in Table 26, items Nos. 6-9. They indicate either that some of the acid passes through the filter or that a portion is retained so firmly that it cannot be washed out.

The next experiments were made with a coarser thimble, RA98, burned for 2 hours at 1800 deg. F. to partially close the pores. If a slow chemical reaction takes place between the acid and some constituent of the alundum, there should be a loss when the dilute acid is merely allowed to run through the thimble. This was found to be true when 2 cu. cm. portions of $\frac{1}{10}$ normal sulphuric acid (= 9.8 milligrams H_2SO_4) in 100 cu. cm. water were passed through the thimble. A determination of the acidity of the water showed that it had been partially neutralized. The data for the experiments are shown in Table 27. The thimble was then soaked for 1 week in dilute hydrochloric acid, rinsed thoroughly with water and the experiments repeated. A slightly larger percentage of acid was recovered in these tests, but when the sample was allowed to stand in contact with the thimble for 30 minutes a low value was again obtained. These experiments show conclusively that some acid is retained by an alundum thimble and cannot be washed out.

Further experiments showed that a small portion of sulphuric acid vapor passes through a fine alundum thimble when air containing the vapor is drawn through the filter. These results are shown in Table 28.

TABLE 28
PERMEABILITY OF POROUS ALUNDUM (RA98) AND SINTERED GLASS BY SULPHURIC ACID VAPOR

No.	H_2SO_4 Taken milligrams	H_2SO_4 Recovered from Thimble milligrams	H_2SO_4 Passing into 2nd Bottle milligrams	H_2SO_4 Not Evaporated milligrams	Per cent Passing Filter on Basis of Total Evaporated	
1	10.62	4.66	0.56	3.03	7.4	Alundum
2	10.62	7.11	0.45	0.95	9.8	
3	18.92	14.15	0.53	0.68	2.8	
4	18.92	14.70	0.99	1.73	5.8	
5	19.02	11.28	0.24	6.18	1.8	
6	19.88	14.32	....	3.92	10.9	Sintered Glass
7	19.88	15.61	....	3.36	5.5	
8	19.88	16.30	....	1.98	9.8	
9	19.88	16.82	....	1.45	8.7	

The use of alundum thimbles, therefore, for the accurate determination of SO_3 present in flue gases in very small concentrations is definitely excluded.

The effect of these results on the data obtained at the three plants where this method was employed is not great enough to warrant discarding them. A very fine thimble was used for these analyses, and while it is evident that the values for SO_3 may be from 10 to 25 per cent too low, their magnitude is of the correct order and the arguments based upon them remain valid.

The next experiments were tried with sintered glass filters of medium porosity. These were selected because of their strength and inactivity toward sulphuric acid. The neutrality of the glass towards the dilute acid was shown by washing back and forth through the thimble a solution containing 19.88 milligrams of sulphuric acid in 100 cu. cm. water and determining the acid recovered with $\frac{1}{50}$ normal alkali (see Table 27). The retention of acid fog by this thimble was tested in the usual manner by drawing air-sulphuric-acid vapor through the thimble. The results (Table 28) show that the glass filters are no better than alundum filters.

The experiments of Hawley and of Nestell and Anderson showed that a double layer of moist filter paper could be used for removing sulphuric acid mist from smelter gases. The concentration of the mist in these gases is higher than that from the SO_3 in flue gases. In Hawley's test experiments the average percentage recovery of sulphuric acid vapor in air was approximately 94 per cent with 30 to 60 milligrams of acid vapor. Nestell and Anderson found even greater accuracy with the quantity of acid vapor ranging from 23 to 577 milligrams of SO_3. These tests were repeated using small quantities of

acid and large quantities of air so that the average concentration of SO_3 in the gases was about 0.005 per cent (6 milligrams per cu. ft.). The recovery of the acid in the double thickness of moist filter paper was only 69 per cent of the total acid evaporated and 3.1 per cent passed through to a second filter. Although moist gases were used for the tests, the remaining 28 per cent of the acid was not recovered. These results are the average of 4 tests. Although they probably could be improved upon, it was felt that the method is inherently wrong for low concentrations of SO_3 because of the possibility of loss of the acid either as vapor or as very small liquid particles.

4. *Absorption of Oxides of Sulphur from Gases and Direct Determination of the Trioxide.*—From the experience of those who have previously worked on this subject there is little doubt that SO_2 is oxidized to some extent when gases containing both oxygen and SO_2 are drawn through water. The rate of oxidation depends upon the extent and character of impurities in the water that may act as catalysts. The tests devised to prove that this oxidation does take place consisted in drawing a mixture of air and a known volume of SO_2 through 50 cu. cm. of standard $\frac{1}{50}$ normal sodium hydroxide solution. The solution was then titrated with standard acid to the methyl orange end-point. Since this end-point is attained when the excess sodium hydroxide is neutralized and the sodium sulphite is converted to sodium bisulphite ($NaHSO_3$), the cu. cm. of base neutralized multiplied by the factor 4.378* should give the cu. cm. of SO_2 absorbed. After titration the solution was treated with neutral hydrogen peroxide to convert the sulphite to sulphate. Titration with alkali to the methyl orange end-point then indicated the volume of base neutralized by SO_2 in the formation of sulphate. This volume in cu. cm. multiplied by the factor 2.189 should be equal to the value obtained by the first titration if no oxidation has taken place. The values obtained were as follows:

SO_2 taken, cu.cm.	87.5	86.8
SO_2 found without H_2O_2, cu.cm.	146.7	141.7
SO_2 found with H_2O_2, cu.cm.	86.1	87.7
Per cent oxidation	67.6	63.3

These results show that any method that depends upon the simultaneous absorption of the gases for the determination of SO_2 and SO_3 will give erroneous results because of oxidation of the former, unless an inhibitor is used.

*The gram molecular volume of SO_2 from the density under standard conditions is 21 888 cu. cm. Internat. Crit. Tables, vol. 3, p. 3.

The oxidation of sodium sulphite solutions has been thoroughly studied recently by Alyea and Bäckström.* They found that the presence of certain alcohols inhibits the oxidation to a large extent, even in the presence of small amounts of catalysts. Of these inhibitors, benzyl alcohol and hydroquinone are the strongest. The latter is excluded from consideration here because of the deep color formed in alkaline solutions. Stannous chloride also cannot be used because of its hydrolysis in these solutions which makes subsequent titration with acid difficult. In order to test the inhibiting power of benzyl alcohol it was necessary to use an analytical method for determining small quantities of sulphate in the presence of large quantities of sulphite and one which also would not require a warm solution or standing over any period of time for precipitation. Such a method could be used for the direct determination of the SO_3 absorbed in a solution and from this value and that of the total sulphur both SO_2 and SO_3 could be readily determined.

The volumetric benzidine method first described by W. Muller† fits these specifications admirably. It consists in adding an excess of benzidine hydrochloride solution to the mixture, filtering and washing the precipitated benzidine sulphate, suspending it in water, and titrating the suspension with $\frac{1}{50}$ normal sodium hydroxide to the phenolphthalein end-point.

The experimental tests on the accuracy of this method for determining the concentration of SO_2 and SO_3 in dilute mixtures of these gases in air were made by drawing the mixture through a coarse sintered glass bubbler in 50 cu. cm. of standard $\frac{1}{5}$ normal sodium hydroxide. The solution was then titrated with standard $\frac{1}{5}$ normal hydrochloric acid to the end-point of brom-cresol-green, an indicator recommended by Alyea, at which the sulphite is completely changed to bisulphite. This titration gives the value of $\frac{1}{2}\ SO_2 + SO_3$. The SO_3 was then determined immediately by the benzidine method. The results are shown in Table 29.

5. *Application of Benzyl Alchohol-Benzidine Method to Flue Gases.*—The results obtained in the tests indicate that the determination of small quantities of SO_3 in the presence of large quantities of SO_2 in SO_3–SO_2–gas mixtures can be carried out by this method. The maximum errors of the SO_2 and SO_3 determination are probably not

*H. N. Alyea and H. L. J. Bäckström, Jour. Am. Chem. Soc., vol. 51, p. 90, 1929.
†See Treadwell and Hall, "Quantitative Analysis," p. 609, 2nd ed., John Wiley and Sons, New York, 1928.

TABLE 29

DETERMINATION OF SO_2 AND SO_3 IN GAS-AIR MIXTURES WITH BENZYL ALCOHOL INHIBITOR AND THE BENZIDINE METHOD

No.	SO_2 Taken cu. cm.	SO_2 Found cu. cm.	Error per cent	SO_3 Taken milligrams	SO_3 Found milligrams	Error per cent
1	88.3	85.3	−3.4	19.93	20.10	+0.8
2	88.5	88.5	0.0	19.93	20.15	+1.1
3	87.8	89.6	+2.1	0.00	0.19	.....
4	85.8	88.4	+3.0	32.85	33.39	+1.6
5	90.9	89.4	−1.6	32.35	30.92	−4.4
6	85.1	85.2	+0.1	30.65	31.55	+2.9
7	86.1	84.8	−1.5	29.04	28.58	−1.6
			Av. ±1.7			Av. ±2.1

greater than 5 per cent. Furthermore, a small error in the SO_2 value does not affect the accuracy of the SO_3 determination, as is the case in most indirect determinations suggested for these gases. The method has the advantage of being quickly and easily carried out. The apparatus necessary to take into the power plant is small. The solutions, with the exception of the benzyl alcohol and benzidine, are common to all laboratories and the exceptions can be obtained easily. The method has been used for making a survey of the gases at two power plants, and the results that were obtained were all that could be desired, and were much more accurate and more easily obtained than those by the filter method.

In using the method the usual precautions for sampling flue gases should be observed. In addition to these, the gases should not come into contact with any metal after they are cooled below the dew-point. For sampling gases in economizers and preheaters a ½-in. pipe of any desired length may be used. A 12-mm. Pyrex tube inserted through a packing gland at the outer end of the pipe should extend several inches inside the setting. The glass bubbler in the absorption bottle may be joined to this with rubber tubing, providing the ends of the glass tubes make contact with each other. A tuft of glass wool placed before the end of the glass tube in the iron pipe should be used to filter out any dust carried by the gas sample.

The gases are drawn from the sampling tube through a 250 cu. cm. wide-mouth bottle containing exactly 50 cu. cm. of standard ⅕ normal sodium hyroxide and 3 cu. cm. of benzyl alcohol. A sintered glass immersion filter of medium porosity serves to break up the bubbles and bring about rapid absorption of SO_2 and SO_3. The gases

may be drawn by means of an aspirator and measured with a flow meter of the orifice type. If this combination is used it is necessary to keep the rate of flow constant by adjusting a relief valve ahead of the aspirator. The volume of gases drawn is computed from the average rate of flow and the time of sampling. In many cases, however, it will be found more convenient to draw the gases through the absorption bottle by means of a small rotary booster pump. The exhaust of the pump is connected to a wet-test gas-meter and the volume of the flue gases read directly. The size of the sample varies from one cu. ft. for high sulphur gases to 3 cu. ft. for low sulphur gases. The gases may be drawn as fast as 0.2 cu. ft. per min.

After the sample has been drawn the Pyrex tube is removed from the iron pipe and rinsed with distilled water into the absorption bottle. The bubbler should be removed and rinsed. The solution in the absorption bottle should be kept below 80 deg. F. by immersion in cold water while the sample is being drawn. This precaution was found necessary on account of a slight oxidation of the dissolved SO_2 in warm solutions even in the presence of the inhibitor. It is also best not to allow the solution to stand more than 3 hours after sampling before titration. The first titration with standard $\frac{1}{5}$ normal hydrochloric acid is carried out as described.

The solution is then treated with 10–15 cc. of benzidine hydrochloride solution made up as follows: 30 g. of benzidine is shaken with 30 cu. cm. of water; the suspension is then diluted with water to 960 cu. cm. and 40 cu. cm. of concentrated hydrochloric acid added which should completely dissolve the benzidine. A silky precipitate of benzidine sulphate forms a few seconds after the solution is added. The solution is allowed to stand for about 10 min. and is then filtered by suction. The precipitate is washed four times with 5 cu. cm. of water each time. Care should be taken not to use too much water because the sulphate is slightly soluble. The precipitate and filter paper are then placed in a flask containing 50 cu. cm. of water and the latter heated to boiling. The suspension is titrated with $\frac{1}{50}$ normal sodium hydroxide using phenolphthalein as the indicator. The benzidine sulphate precipitate dissolves rather slowly so that care must be taken to see that is it all dissolved. A good procedure is to add sufficient sodium hydroxide so that the red color of the basic solution remains after boiling for three minutes. The solution is then cooled and titrated to the end-point with $\frac{1}{50}$ normal acid in the usual manner.

The calculations are made as follows:

$$\text{Per cent } SO_3 \text{ by volume} = \frac{\text{cu. cm. N/50 NaOH} \times 0.000791^*}{\text{corrected volume flue gas in cu. ft.}}$$

$$\text{Per cent } SO_2 \text{ by volume} = \frac{2\left[(50.00 - \text{cu.cm. N/5 HCl}) - \frac{\text{cu. cm. N/50 NaOH}}{10}\right] \times 0.00791^*}{\text{corrected volume flue gas in cu. ft.}}$$

The corrections to the volume of flue gas are those of temperature, barometric pressure and vapor pressure of water. The values may be converted to grains per cu. ft. as follows:

$$\text{Grains } SO_2 \text{ per cu. ft.} = \text{per cent } SO_2 \times 12.48$$
$$\text{Grains } SO_3 \text{ per cu. ft.} = \text{per cent } SO_3 \times 15.60$$

*These values are based on the molecular volume of an ideal gas.

APPENDIX B

Theory of Corrosion

1. *Literature on Corrosion.*—Corrosion may be defined as the loss of metal due to the chemical action of external agencies. The conversion of the metal into one of its chemical compounds usually results in the loss of those physical properties that are essential to its usefulness. In many respects the metals used for structural purposes are chemically quite active. For this reason a great many reactions may take place that may be classed as corrosion reactions. Furthermore, the number of factors influencing any one reaction that may determine the rate of corrosion is large. Because of the diversity of its causes, therefore, and of its importance, corrosion has been a popular subject for research by both chemists and engineers. V. V. Kendall of the National Tube Company in 1926 compiled an unpublished bibliography of 7000 classified articles on corrosion. It would be beyond the scope of this bulletin to present even an outline of the work which has been done on the general subject. Reference may be made, however, to a few of the outstanding treatises on the subject. Of these, the work of U. R. Evans* is most distinctive from the fundamental side. This author has done much to clear up some of the questions that have arisen in connection with the modern theory. On the more or less practical side, F. N. Speller† of the National Tube Company has written an excellent book on the causes and prevention of corrosion. Other treatises worthy of notice are those by Pollitt‡ and by Friend.§ Reference to these will be highly instructive to anyone engaged in the study of corrosion.

A. Electrochemical Theory of Corrosion

2. *Primary Corrosion Reactions.*—The theory of corrosion has long been a matter of discussion. There has been much difference of opinion as to the reactions involved. With the application of sound chemical principles to the subject, however, many of the differences have been cleared up and the general ideas of the causes of corrosion are almost universally accepted. While discussing the specific subject of corrosion by flue gases it will be well to outline these ideas in order that a clearer and more concise viewpoint may be had in the discussion.

*U. R. Evans, "The Corrosion of Metals," Edward Arnold Book Co., London, 1924.
†F. N. Speller, "Corrosion, Causes and Prevention," McGraw-Hill Book Co., New York, 1926.
‡A A. Pollitt, "The Causes and Prevention of Corrosion," D. Van Nostrand Co., New York, 1924.
§J. N. Friend, "The Corrosion of Iron and Steel," Longmans-Green and Company, 1911.

Of the various theories that have been proposed, that of the electrochemical action adapts itself to most of the facts. As it stands, it applies only to under-water corrosion. As will be shown later, however, it can be extended to gaseous corrosion, especially that which occurs in the range of temperature where liquid films may exist.

The electrochemical theory is based on Nernst's theory of the solution potentials of metals and on the ionization theory of acid, bases, and salts first postulated by Arrhenius. The former states that when a metal is in contact with a liquid there is a certain potential tending to drive the metal into solution in the form of its ions with the liberation of electrons at the surface of the metal. This tendency may be expressed by

$$\text{Metal} \rightleftarrows \text{Metal ions}^{n+} + n\,e. \tag{1}$$

Here n represents the valence of the ion and e the electron, or unit of negative electricity. For the specific case of iron,

$$\text{Fe} \rightleftarrows \text{Fe}^{++} + 2\,e. \tag{1a}$$

The reaction is reversible and the accumulation of either electrons on the metal or of the metal ions in the solution will create an opposing tendency which will tend to establish an equilibrium.

If there are conditions present which tend to disturb this primary action the equilibrium will be displaced and either more or less metal will pass into solution according to the nature of the conditions. For instance, if there are other ions present that have a tendency to combine with the electrons, the equilibrium is shifted to the right because of the reaction

$$\text{Ion}^{n'+} + n'e \rightleftarrows \text{molecule} \tag{2}$$

For example,

$$\text{H}^+ + e \rightleftarrows \text{H}. \tag{2a}$$

The same result can be produced in the removal of the electrons by imposing a positive potential on the metal. Corrosion reactions, therefore, are primarily electrochemical in nature, the total result being the exchange of electrons from the metal to some ion in the solution. Summarizing by combining Equations (1a) and (2a) for the action of hydrogen ions on iron,

$$\text{Fe} + 2\text{H}^+ \rightleftarrows \text{Fe}^{++} + 2\text{H} \tag{3}$$

3. *Secondary Corrosion Reactions.*—In the same way that the removal of the electrons from the metal accelerates the corrosive attack so will the removal of the metal ions, or of the resulting molecu-

lar species, also increase the amount of metal passing into solution. Thus any of the following reactions will increase the corrosion of iron: (a) the precipitation of ferrous hydroxide, (b) the evolution of hydrogen gas, (c) the reaction of hydrogen with oxygen to form water. These are expressed by the equations:

$$Fe^{++} + 2\ OH^{-} \rightleftarrows Fe(OH)_2 \text{ (dissolved)} \rightleftarrows Fe(OH)_2\text{(solid)} \quad (4a)$$

$$2H \rightleftarrows H_2 \text{ (dissolved)} \rightleftarrows H_2 \text{ (gas)} \quad (4b)$$

$$2H + \tfrac{1}{2}O_2 \rightleftarrows H_2O \quad (4c)$$

4. *Single Electrode Potentials.*—The solution potentials of metals differ greatly. The more active metals, such as sodium, magnesium and zinc, have a high solution potential, while the more noble metals, such as gold and platinum, have a very low solution potential. In Table 30 are recorded the solution potentials of several elements. These values are stated in terms of volts and may actually be measured as such. They represent the potential of the metal immersed in a solution in which the active concentration, or activity, of the metallic ions is unity.*

Included in Table 30 are values of reactions somewhat similar to the solution of a metal. These are the reduction potentials of ions. They represent the tendency for an ion to change from one state of valence to another. This may be represented by

$$\text{Metal ions}^{n+} \rightleftarrows \text{metal ions}^{m+} + (m-n)e \quad (5)$$

where m is greater than n.

Taking any two of the values given in the table, the tendency for a reaction to take place between the two members will be the algebraic difference of the values. For example,

$$Fe \rightarrow Fe^{++} + 2\,e \qquad E^0 = \ \ 0.441 \quad (6a)$$

$$Cu \rightarrow Cu^{++} + 2\,e \qquad E^0 = -0.349 \quad (6b)$$

Subtracting

$$Fe + Cu^{++} \rightarrow Fe^{++} + Cu \qquad E^0 = \ \ 0.790 \quad (6c)$$

*In order to avoid confusion, the term "active concentration" will be used in place of "activity." It will be designated by the symbol C. The active concentration, or activity, of the ions of a strong electrolyte is a function of the gross concentration of the dissolved substance, i.e., $C_+ = \gamma_+ m_+$ and $C_- = \gamma_- m_-$, where C, γ, and m refer respectively to the activity, the activity coefficient, and the gross concentration of the ions, the + and − signs referring to the positive and negative ions. In this case the gross concentration is measured in moles (ionic weights) per 1000 grams of water. The value of the activity coefficient, γ, depends on the nature of the individual ion, and on the total concentration of ions in the solution. The actual values, in general, vary from 0.1 to 1, and may greatly exceed unity, according to these conditions. Unit active concentration is different, therefore, from unit gross concentration and may differ from it by as much as several hundred per cent. For a more complete discussion of this subject cf. Eucken, Jette and LaMer, "Fundamentals of Physical Chemistry," pp. 315-349, McGraw-Hill Book Co., New York, 1925.

TABLE 30
SINGLE ELECTRODE POTENTIALS OF VARIOUS METALS AND IONS AT UNIT ACTIVE CONCENTRATION AND 25 DEG. C.*

Substance	Product	Reaction	Electrode Potential Volts (E^0)
Sodium	Sodium ions	$Na \rightarrow Na^+ + e$	2.7125
Magnesium	Magnesium ions	$Mg \rightarrow Mg^{++} + 2e$	1.866†
Zinc	Zinc ions	$Zn \rightarrow Zn^{++} + 2e$	0.7581
Iron	Ferrous ions	$Fe \rightarrow Fe^{++} + 2e$	0.441
Nickel	Nickel ions	$Ni \rightarrow Ni^{++} + 2e$	0.22†
Tin	Stannous ions	$Sn \rightarrow Sn^{++} + 2e$	0.136
Lead	Plumbous ions	$Pb \rightarrow Pb^{++} + 2e$	0.122
Hydrogen	Hydrogen ions	$H_2 \rightarrow 2H^+ + 2e$	0.000
Copper	Cupric ions	$Cu \rightarrow Cu^{++} + 2e$	−0.3448
Hydroxyl ions	Oxygen	$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$	−0.3976
Ferrous ions	Ferric ions	$Fe^{++} \rightarrow Fe^{+++} + e$	−0.7477‡
Silver	Silver ions	$Ag \rightarrow Ag^+ + e$	−0.7995
Chloride ions	Chlorine	$2Cl^- \rightarrow Cl_2 + 2e$	−1.3594
Cobaltous ions	Cobaltic ions	$Co^{++} \rightarrow Co^{++++} + 2e$	−1.76†

*Unless otherwise noted these values are taken from Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," p. 433, McGraw-Hill Book Co., New York, 1923.
†Creighton and Fink, "Electrochemistry," vol. 1, p. 229, John Wiley and Sons, 1924.
‡Popoff and Kunz, Jour. Am. Chem. Soc., vol. 51, p. 382, 1929.

The voltages given will be the electromotive force of a cell composed of strips of the metals dipping in solutions of their respective ions at unit active concentration, the solutions being connected by a salt bridge. The same reaction will take place when iron is immersed in copper ions of unit active concentration. The energy change in the latter case is dissipated as heat and as entropy. The relation between the maximum available energy of the reaction and the potential of the cell is

$$\Delta F = -n FE^0 \qquad (7)$$

where ΔF is the free, or available, energy,

n is the number of electrons involved,

F is the capacity term, the faraday.

Following the usual custom of thermodynamics the energy evolved by a reaction is considered as negative.

It will be seen that there is a tendency for a substance to give electrons to the ion of any substance below it in the table and that this tendency is greater the farther the two are separated in the table. Iron reacts with nickel ions, lead ions, hydrogen ions, copper ions, oxygen, ferric ions, etc., but not with zinc ions or with sodium ions. *These statements all refer to unit, or to any other equal active concentration of the ions.*

5. *Effect of Concentration of Ions on Solution Potential of Metal.*— The effect of the concentration of the ion on the electrode potential may be stated by the equation:

$$E = E^0 - \frac{RT}{nF} \log_e C_{\text{ion}} \tag{8}$$

E represents the electrode potential at the active concentration of ions considered
E^0 the electrode potential at unit active concentration
R the gas constant (1.98 calories)
F the faraday (96 494 coulombs)
T the temperature in deg. abs.
n the number of electrons involved in the change
$\log_e$ the natural logarithm
C_{ion} the active concentration of the ion considered.
(At 25 deg. C., $\frac{RT}{F} \log_e C_{\text{ion}} = 0.059 \log_{10} C_{\text{ion}}$. Unless otherwise indicated this temperature and value will be used in order to simplify the derivations.)

Thus an increase in the active concentration of the ion tends to decrease the tendency for the metal to pass into solution while a decrease in active concentration would have the opposite effect.

For any active concentration of the ions the tendency for a metal to react with the ions of another metal becomes

$$\begin{aligned} E_{\text{total}} &= E_1 - E_2 \\ &= E^0_1 - E^0_2 - \frac{0.059}{n} \log C_1 + \frac{0.059}{n} \log C_2 \end{aligned} \tag{9}$$

Thus, when a strip of iron and a strip of copper are immersed in solutions of their respective ions, the active concentrations of which are respectively 0.01 and 0.1, and the two metals are connected by an electrical conductor, the potential of the cell will be

$$E = 0.441 + 0.349 - \frac{0.059}{2} \log 0.01 + \frac{0.059}{2} \log 0.1 \tag{9a}$$

$$= 0.920 \text{ volts.}$$

The energy liberated will be

$$\Delta F = -0.920 \times 2 \times 96\ 494$$

$$= -177\ 550 \text{ calories.}$$

Current will continue to flow, with iron going into solution and copper ions coming out, until $E = 0$, or until

$$\log C_{Fe^{++}} - \log C_{Cu^{++}} = 29.8 \tag{9b}$$

and

$$\frac{C_{Fe^{++}}}{C_{Cu^{++}}} = 10^{30}$$

Except for the difference in the form of the energy liberated, exactly the same thing would occur if the iron had been placed in a solution of ferrous and cupric ions of the given concentrations. We should judge, therefore, that cupric ions are corrosive to iron. The same conclusion must be reached for various concentrations of other ions below and slightly above iron in Table 30.

6. *Effect of Pressure on Solution Potential of Gases.*—In the case of gases, one other factor enters into the conditions determining the solution potential, viz., the pressure of the gas. The relation is expressed by

$$E = E^0 + \frac{0.059}{n} \log P_{gas} \tag{10}$$

7. *Corrosion of Metals by Hydrogen Ions.*—Inasmuch as most solutions are composed of water in which hydrogen ions are always present, an estimate of the effect of the hydrogen ion concentration on the corrosion of metals can now be made. The general equation for the action is

$$Me + nH^+ \rightarrow Me^{n+} + n/2\ H_2$$

The potential of the cell, which is a measure of the tendency to corrode, is represented by

$$E = E^0_{Me} - E^0_{H_2} - \frac{0.059}{n} \log C_{Me^{n+}} + \frac{0.059}{n} \log (C_{H^+})^n - \frac{0.059}{n} \log (p_{H_2})^{n/2}$$

$$= E^0_{Me} - E^0_{H_2} - \frac{0.059}{n} \log \left\{ \frac{(p_{H_2})^{n/2} \times C_{Me^{n+}}}{(C_{H^+})^n} \right\} \tag{11}$$

At equilibrium, when no further attack can take place,

$$E = 0,$$

$$\text{or } \frac{0.059}{n} \log \frac{(p_{H_2})^{n/2} \times C_{Me^{n+}}}{(C_{H^+})^n} = E^0_{Me} - E^0_{H_2} \tag{11a}$$

TABLE 31

ACTIVE CONCENTRATION OF VARIOUS METALLIC IONS NECESSARY FOR EQUILIBRIUM WITH THE METAL AT VARIOUS CONCENTRATIONS OF HYDROGEN IONS AND PRESSURES OF HYDROGEN AT 25 DEG. C.

Pressure Hydrogen Atmospheres	Active Concentration—Ionic Weights per Liter			
	C_{H^+}	$C_{Zn^{++}}$	$C_{Fe^{++}}$	$C_{Cu^{++}}$
1	1	5.0×10^{25}	8.9×10^{14}	1.3×10^{-12}
1	10^{-2}	5.0×10^{21}	8.9×10^{10}	1.3×10^{-16}
1	10^{-4}	5.0×10^{17}	8.9×10^{6}	1.3×10^{-20}
1	10^{-6}	5.0×10^{13}	8.9×10^{2}	1.3×10^{-24}
1	10^{-8}	5.0×10^{9}	8.9×10^{-2}	1.3×10^{-28}
1	10^{-10}	5.0×10^{5}	8.9×10^{-4}	1.3×10^{-32}
1	10^{-12}	50	8.9×10^{-8}	1.3×10^{-36}
10^{-1}	10^{-2}	5.0×10^{22}	8.9×10^{11}	1.3×10^{-15}
10^{-5}	10^{-2}	5.0×10^{28}	8.9×10^{15}	1.3×10^{-11}
10^{-10}	10^{-2}	5.0×10^{31}	8.9×10^{20}	1.3×10^{-6}
2.3×10^{-42}	10^{-2}	2.2×10^{63}	3.9×10^{52}	8.9×10^{25}

In Table 31 values are shown for the active concentration of zinc, ferrous, and cupric ions in equilibrium with the metal and hydrogen ions for different pressures of hydrogen and concentrations of hydrogen ions. The values represent the limiting concentration of the metallic ions at which corrosion will cease. If the solubility of the salt or of the hydroxide is such that the value indicated cannot be attained because of the precipitation the corrosion should proceed indefinitely. As might be expected, the concentration of cupric ions resulting from corrosion is extremely small in all cases. Copper, therefore, is not corroded by acids unless secondary reactions occur. An example will be seen in the corrosion of copper in the presence of oxygen.

8. *Corrosion of Metals by Oxygen.*—It is apparent from Table 30 that the tendency for metals to react with dissolved oxygen is even greater than that with hydrogen ions. The reaction may be represented by

$$\mathrm{Me} + \frac{n}{4}\mathrm{O_2} + \frac{n}{2}\mathrm{H_2O} \rightarrow \mathrm{Me}^{n+} + n\mathrm{OH}^-$$

The potential can be represented as before by the relation

$$E = E^0_{\mathrm{Me}} - E^0_{\mathrm{O_2}} - \frac{0.059}{n}\log C_{\mathrm{Me}^{n+}} - \frac{0.059}{n}\log (C_{\mathrm{OH}^-})^n + \frac{0.059}{n}\log (p_{\mathrm{O_2}})^{n/4}$$

$$= E^0_{\mathrm{Me}} - E^0_{\mathrm{O_2}} - \frac{0.059}{n}\log \left\{\frac{C_{\mathrm{Me}^{n+}} \times (C_{\mathrm{OH}^-})^n}{(p_{\mathrm{O_2}})^{n/4}}\right\} \qquad (12)$$

TABLE 32
ACTIVE CONCENTRATION OF VARIOUS METALLIC IONS NECESSARY FOR EQUILIBRIUM WITH THE METAL AT VARIOUS CONCENTRATIONS OF HYDROGEN IONS AND PRESSURES OF OXYGEN AT 25 DEG. C.

Pressure Oxygen Atmospheres	Active Concentration—Ionic Weights per Liter			
	C_{H^+}	$C_{Zn^{++}}$	$C_{Fe^{++}}$	$C_{Cu^{++}}$
1	1	1.5×10^{67}	2.8×10^{56}	2.6×10^{29}
1	10^{-2}	1.5×10^{63}	2.8×10^{52}	2.6×10^{25}
1	10^{-4}	1.5×10^{59}	2.8×10^{48}	2.6×10^{21}
1	10^{-6}	1.5×10^{55}	2.8×10^{44}	2.6×10^{17}
1	10^{-8}	1.5×10^{51}	2.8×10^{40}	2.6×10^{13}
1	10^{-10}	1.5×10^{47}	2.8×10^{36}	2.6×10^{9}
1	10^{-12}	1.5×10^{43}	2.8×10^{32}	2.6×10^{5}
0.209	10^{-2}	7.0×10^{63}	1.3×10^{52}	1.2×10^{25}
10^{-2}	10^{-2}	1.5×10^{62}	2.8×10^{51}	2.6×10^{24}
10^{-4}	10^{-2}	1.5×10^{61}	2.8×10^{50}	2.6×10^{23}
10^{-10}	10^{-2}	1.5×10^{58}	2.8×10^{47}	2.6×10^{20}

At equilibrium, when corrosion ceases, and $E = 0$

$$\frac{0.059}{n} \log \left\{ \frac{C_{Me^{n+}} \times (C_{OH^-})^n}{(p_{O_2})^{n/4}} \right\} = E^0_{Me} - E^0_{O_2} \qquad (12a)$$

In aqueous solutions

$$C_{H^+} \times C_{OH^-} = K,$$

where K is a constant, the value of which is 10^{-14} at 25 deg. C. Substituting the active hydrogen ion concentration in Equation (12a),

$$\frac{0.059}{n} \log \left\{ \frac{C_{Me^{n+}} \times 10^{-14n}}{(p_{O_2})^{n/4} \times (C_{H^+})^n} \right\} = E^0_{Me} - E^0_{O_2} \qquad (12b)$$

Values for the concentration of zinc, ferrous, and cupric ions in equilibrium with solutions containing dissolved oxygen and hydrogen ions have been calculated from Equation (12b) and are shown in Table 32. Since the partial pressure of oxygen in the atmosphere is approximately 0.209 atmospheres, the large concentration of metal ions required shows that dissolved oxygen has far more corrosion tendency than hydrogen ions and that even a strongly alkaline solution does not remove this tendency.

9. *Corrosion by Ferric Ions.*—A reaction similar to that of oxygen on metals may be brought about by ferric ions:

$$Me + nFe^{+++} \rightarrow Me^{n+} + nFe^{++}.$$

$$E = E^0_{Me} - E^0_{Fe^{++}} - \frac{0.059}{n} \log \frac{(C_{Fe^{++}})^n \times C_{Me^{n+}}}{(C_{Fe^{+++}})^n} \qquad (13)$$

TABLE 33
ACTIVE CONCENTRATION OF VARIOUS METALLIC IONS NECESSARY FOR EQUILIBRIUM WITH THE METAL AT VARIOUS RATIOS OF FERRIC TO FERROUS IONS AT 25 DEG. C.

Ratio $\frac{Fe^{+++}}{Fe^{++}}$	Active Concentration—Ionic Weights per Liter		
	$C_{Zn^{++}}$	$C_{Fe^{++}}$	$C_{Cu^{++}}$
10^{-3}	1.1×10^{35}	2.0×10^{24}	4.6×10^{-3}
10^{-6}	1.1×10^{39}	2.0×10^{28}	4.6×10
10^{-4}	1.1×10^{43}	2.0×10^{32}	4.6×10^{5}
10^{-2}	1.1×10^{47}	2.0×10^{36}	4.6×10^{9}
1	1.1×10^{51}	2.0×10^{40}	4.6×10^{13}
10^{2}	1.1×10^{55}	2.0×10^{44}	4.6×10^{17}
10^{4}	1.1×10^{59}	2.0×10^{48}	4.6×10^{21}

At equilibrium, $E = 0$

$$\log \frac{(C_{Fe^{++}})^n \times C_{Me^{n+}}}{(C_{Fe^{+++}})^n} = \frac{n(E^0_{Me} - E^0_{Fe^{+++}})}{0.059} \qquad (14a)$$

Values for the active ion concentrations at different ratios of Fe^{+++}/Fe^{++} are given in Table 33. Evidently ferric salts will cause corrosion, particularly of copper and the copper alloys that are not attacked by ordinary acids.

10. *Conception of an Oxygen Carrier.*—In the preceding derivations only the potential corrosive power of the various ions could be forecast. The actual kinetics of the reaction and the rate with which it occurs cannot be predicted from thermodynamics alone. In many cases, the power to react is obscured by other factors. For instance, even the action of oxygen is not as rapid as that of some of less potential corrosive substances. In many cases, a polarization occurs from the accumulation of the corrosion products. The action of some substances seems to be increased by the presence of oxygen. In the action of acids on iron, Whitman, Russell, and Altieri* have shown that, for as low a concentration as $C_{H^+} = 10^{-4}$, hydrogen gas is liberated. Below this concentration no bubbles of the gas are evolved, and the reaction will cease because of the accumulation of atomic hydrogen if no oxygen is present. Apparently with oxygen present the hydrogen is removed by the reaction

$$2\,H + \tfrac{1}{2}O_2 \rightarrow H_2O.$$

*Whitman, Russell, and Altieri, Ind. Eng. Chem., vol. 16, p. 665, 1924.

Below $C_{H^+} = 10^{-4}$, therefore, the rate of corrosion often depends on the amount of oxygen dissolved in the solution. In such a corrosion reaction the hydrogen may be regarded as an "oxygen carrier," for the ultimate result is the action of the oxygen on the iron through the medium of hydrogen ions.

The reaction tendency between dissolved hydrogen and dissolved oxygen may be estimated by methods similar to those used for the metals and ions:

$$H \rightleftarrows 2\,H^+ + 2\,e$$

$$2\,OH^- \rightleftarrows H_2O + \tfrac{1}{2}\,O_2 + 2\,e$$

Subtracting,

$$H_2 + \tfrac{1}{2}\,O_2 + H_2O \rightleftarrows 2\,H^+ + 2\,OH^-$$

For a reversible oxygen-hydrogen cell at 25 deg. C., therefore,

$$E = E^0_{H_2} - E^0_{O_2} - \frac{0.059}{2}\log (C_{H^+})^2 + \frac{0.059}{2}\log p_{H_2}$$

$$- \frac{0.059}{2}\log C^2_{OH^-} + \frac{0.059}{2}\log (p_{O_2})^{\frac{1}{2}} \qquad (15)$$

At equilibrium $E = 0$, or

$$\frac{0.059}{2}\log \frac{C^2_{H^+} \times C^2_{OH^-}}{p_{H_2} \times (p_{O_2})^{\frac{1}{2}}} = E^0_{H_2} - E^0_{O_2} \qquad (15a)$$

Substituting $C_{H^+} \times C_{OH^-} = 10^{-14}$

$$E^0_{H_2} = 0$$

$$E^0_{O_2} = -0.3976$$

and solving,

$$\log \{p_{H_2} \times (p_{O_2})^{\frac{1}{2}}\} = -41.4780 \qquad (15b)$$

In solutions in equilibrium with the air at ordinary pressures

$$p_{O_2} = 0.209 \text{ atmospheres}$$

whence $$p_{H_2} = 2.3 \times 10^{-42} \text{ atmospheres.} \qquad (15c)$$

The removal of the hydrogen by reaction with the dissolved oxygen to such an extent would cause the attack of acids on most metals to be severe. This was shown in Table 31.

An even better example of an "oxygen carrier" is afforded by ferric ions. If the solution is supplied with oxygen at a pressure of 0.209 atmospheres the ratio Fe^{+++}/Fe^{++} tends to remain extremely

high,* due to the oxidation of ferrous ions. Consequently, solutions of ferric salts in the presence of oxygen are often severely corrosive.

Such explanations throw an important light on the atmospheric and gaseous corrosion of iron at temperatures below the dew-point. Furthermore, they explain the old adage that "rust begets rust." In Chapter IV the accelerating effect of ferric salts on the corrosion of iron by aerated sulphuric acid solutions was shown. The same result has been demonstrated by Hall and Teague in the corrosion of copper alloys and of tin and zinc by acid mine waters.

11. *Overvoltage.*—Another disturbing factor which may enter into the equilibria under discussion is that of overvoltage. This phenomenon, simply stated, is a decrease in the tendency of a metal to pass into solution. The exact cause of overvoltage is not known, but it is supposed that it is due to some surface effect such as an accumulation of hydrogen (or other gas) which would tend to oppose the solution tendency of the metal to a certain extent. Since the hydrogen overvoltage on iron is equal to 0.27 volts, a smaller concentration of ferrous ions will prevent iron from passing into solution.

If overvoltage is due to the concentration of hydrogen on the electrode, anything that will remove this hydrogen will tend to reduce the overvoltage and, therefore, increase the tendency for the metal to pass into solution. Thus, the presence of oxygen or any oxidizing agent will cause a greater attack on the metal by the hydrogen ions.

12. *Conception of Controlling Factor.*—Of the series of reactions which take place in the process of corrosion, that which is slowest will necessarily be the one which will determine the rate at which the total reaction proceeds. For example, if the actual diffusion of the oxygen to the metal is extremely slow compared to the other reactions, the rate of corrosion will depend upon the rate of diffusion. On the other hand, if the concentration of hydrogen ions is great enough for hydrogen gas to be evolved, the presence of oxygen is not necessary for the corrosion, and the attack will be independent of the rate of diffusion. For this reason the factors controlling the rate of corrosion will vary from case to case, and *before any statement can be made as to the cause of the corrosion it is necessary to know something of the conditions.*

13. *Factors Affecting Rate of Corrosion.*—As examples of other factors that may control the rate of corrosion, the following may

*At 25 deg. C., $\frac{C_{Fe^{+++}}}{C_{Fe^{++}}} = 5.8 \times 10^{(19-p_H)}$, where $p_H = \log \frac{1}{C_{H^+}}$

be cited: The temperature influences the rate of corrosion, since the speed of most chemical reactions is increased by an increase in temperature. The rate of diffusion and, therefore, the viscosity of the solution will determine the rate at which the ions are removed from the metal surface, and at which the oxygen is brought in. The thickness of the layer of solution through which the diffusion must take place will also determine the concentration of oxygen on the surface. Mechanical stress increases the solution tendency of many metals. Stray electric currents may have the same effect. The presence of a second metal, as in an alloy, may influence the same factor. The character of the metal surface may also be a controlling factor. Certain metals have a property known as passivity, due to the formation of a thin protective coating of some sort that prevents attack upon them by outside agencies. In many cases passivity is produced by a product of the corrosion. To some extent iron oxide or rust will tend to prevent corrosion, especially if the coating is continuous over the entire surface of the metal. The presence of dissolved substances in the solution usually affects the solubility of the corrosion product. It is to be expected, therefore, that those which reduce the solubility would tend to reduce corrosion, other things being equal.

In the foregoing discussion the entire metal surface was considered as being uniform. Such reactions as those described would produce a uniform corrosion if every spot in the metal and in the solution were identical. In the event that the metal or solution is not homogeneous, corrosion may take place more severely at one point than another and localized corrosion, or pitting, will result. Since it is not the total loss of metal but the rate of penetration that determines the service time, pitting may be more disastrous than uniform corrosion. Evans has shown that if part of a metal surface is protected from oxygen while another part is unprotected, the protected part will be more severely attacked than the unprotected part. For this reason the presence of adhering particles of mill scale will often lead to severe pitting. In the same way, since the hydroxides of iron are insoluble, they will tend to protect the surface from oxygen. If the protection is not uniform, corrosion will proceed more rapidly beneath the corrosion product than elsewhere. Hence it is often the case that if corrosion is once started it proceeds to pit the metal severely.

B. Atmospheric and Gaseous Corrosion

14. *Types of Gaseous Corrosion Reactions.*—Corrosion reactions in which the essential attack is that due to a vapor or gas are usually not so severe as those which take place under a liquid. The reasons

for this are apparent after a consideration of the electro-chemical theory, wherein the primary assumptions are the presence of ions and of a solution potential of the metal. In certain cases, however, corrosion by gases may take place so rapidly that its consequences are serious.

Gaseous corrosion reactions may be divided roughly into two groups according to the temperature. At high temperatures, there exists a direct action between certain gases and metals. This attack is a type of slow combustion and takes place in the presence of oxygen, hydrogen sulphide, sulphur dioxide, and various other gases which oxidize iron as well as other metals. The temperature range in which these reactions take place is above 1000 deg. F. At lower temperatures, although the capacity for the action may be larger, actually the rate of attack is smaller. Because of the protective character of the corrosion product, it is seldom that any deterioration is encountered between the temperatures of 400 and 1000 deg. F. In this zone, however, tarnishing often takes places, and while the appearance of metal may be affected, no great changes in its other physical properties are observed.

The second zone of gaseous corrosion is the one which is more often encountered, and corresponds to that in which a liquid film exists on the metal surface. The reactions that take place here are similar in type, at least, to those which take place under water. Certain factors are brought into play, however, by the thinness of the liquid film and these may control the rate of attack. In atmospheric and gaseous corrosion where oxygen is present, there can never be an insufficient quantity of this gas due to the slowness of diffusion, such as might exist under water. Furthermore, the main controlling variables are often those substances the concentration of which determine the dew-point, i.e., the highest temperature at which a liquid film will form. For this reason the action of hydrogen sulphide, sulphur dioxide, and other substances is practically negligible at low temperatures, while a trace of sulphur trioxide, which may cause an extremely high dew-point will cause serious corrosion. This will be true not only because of the sulphuric acid formed by condensation, but also because other substances which may act as oxidizing agents are brought into solution, e.g., ferric ions. The liquid film may not be of any great thickness. In fact, Evans and Vernon have shown that some corrosion occurs when only an absorbed liquid film exists on the surface, and that such a film may form when the moisture in the air is below the saturation point. Because of the different effects

of various substances on the dew-point, it is not surprising that the rate of atmospheric corrosion differs greatly with the composition of the gas. A change of 0.001 per cent in the concentration of sulphur trioxide is sufficient to change the dew-point 20 to 40 deg. F.

Not only the composition of the gas may determine the point at which the liquid film will exist, but also the nature of any solids adhering to the metal surface will often have an effect. If these solids are of a deliquescent nature they tend to absorb moisture from the surrounding gases and form a saturated solution, the aqueous vapor pressure of which is less than that of the surrounding gases. Many salts possess the property of deliquescence, and any of these, when present on a metal surface, would promote corrosion. The rusting of iron is often auto-accelerating because rust itself is a deliquescent substance, and, therefore, once formed, it will tend to create a liquid film on the metal.

The essential differences between the controlling factors in gaseous corrosion at low temperatures and those in under-water corrosion, therefore, are: (1) the inexhaustible supply of oxygen, (2) the influence of various substances on the dew-point, and (3) the effect of deliquescent substances. Once a liquid film is formed, the reactions that take place in the gaseous corrosion are essentially the same as those which take place under water. They are both of an electrochemical nature. In the preceding chapters it was shown that these are the factors which influence the rate of corrosion by flue gases.

APPENDIX C

Reduction of Sulphuric Acid Vapor in Furnace Gases

In Chapter II the reactions undergone during the combustion of the sulphur in coal were discussed. It was shown that sulphur dioxide is the principal product formed and that the conversion of the dioxide to sulphur trioxide is very small. The only place where this reaction may reach important proportions is in saturated solutions of iron sulphate which exist on the surfaces of economizers and preheaters at temperatures below the dew-point of the gases, or hygroscopic point of the solid. These oxidation reactions have an important counterpart when the fuel burned is not coal but petroleum residues, in which the sulphur exists for the most part as sulphuric acid. A presentation of the equilibria which may be obtained in the furnace when such fuel is burned is given here in order to explain the data shown in Table 10 and to point out that it is possible to obtain gases with no more detrimental qualities, so far as the sulphur compounds are concerned, than those of the gases from a high sulphur coal.

In Table 10 it was shown that an average of approximately 85 per cent of the sulphuric acid in the fuel is reduced to sulphur dioxide in the flue gases. Evidently this reduction takes place in a reducing zone in the furnace where the high temperatures together with the hot carbon and carbon monoxide readily convert the sulphuric acid vapor to sulphur dioxide. Since it was shown already that the dioxide is not reoxidized in the cooler portions of the boiler, the type of sulphur compound present in the flue gases depends only on the reactions undergone in the furnace. Sherman and Taylor,* in their investigation of refractories service conditions in pulverized fuel boilers, found that a reducing zone may exist as far as 35 ft. from the burners and that, in this zone, the gases may contain as much as 10 per cent carbon monoxide and 4 per cent hydrogen with no oxygen. Free carbon is present of course in such locations. Under these conditions the reactions that take place with the sulphur trioxide from the sulphuric acid vapor may be represented as follows:

$$SO_3 + \tfrac{1}{2}\,C \rightarrow SO_2 + \tfrac{1}{2}\,CO_2 \qquad (1)$$

sulphur trioxide + carbon → sulphur dioxide + carbon dioxide

*Sherman and Taylor, Trans. Amer. Soc. Mech. Eng., Fuels and Steam Power Section, vol. 50, p. 127, 1928.

and

$$SO_3 + CO \rightarrow SO_2 + CO_2 \qquad (2)$$

sulphur trioxide + carbon monoxide → sulphur dioxide + carbon dioxide

The tendency for these reactions to take place may be calculated by the ordinary thermodynamic methods. Using the data of Lewis and Randall* it may be shown that the free energy change (negative free energy is a measure of the tendency for a reaction to take place spontaneously) for reaction (1) is the following function of the temperature:

$$\Delta F = -24\,455 + 0.30T \log_e T - 0.00032T^2 + 0.00000006T^3 - 23.23T$$

Here ΔF represents the free energy change in calories per gram molecular weight and T is the absolute temperature (= deg. C. + 273). For reaction (2) the free energy equation is

$$\Delta F = -44\,910 + 2.75T \log_e T - 0.0028T^2 + 0.00000031T^3 - 16.90T$$

The values of ΔF for the two reactions have been calculated for several temperatures in the range encountered in a boiler furnace and are shown in Table 34.

A more useful term may be calculated from the values of ΔF, viz.,

$$\Delta F = -RT \log_e K$$

where K represents a constant ratio, which, for reaction (1), is

$$K = \frac{p_{SO_2} \times p_{CO_2}^{\frac{1}{2}}}{p_{SO_3}},$$

and for reaction (2)

$$K = \frac{p_{SO_2} \times p_{CO_2}}{p_{SO_3} \times p_{CO}}$$

R represents the gas constant in terms of calories; p_{SO_2}, etc., represents the partial pressure expressed in atmospheres of SO_2, etc., in the gas. In the present case p_{SO_2}, etc., is related to the volume per cent as follows:

$$p_{SO_2} = \frac{\text{per cent } SO_2}{100}.$$

From the values of ΔF, therefore, it is possible to calculate the

*Lewis and Randall, *loc. cit.*, p. 551, 576.

TABLE 34

FREE ENERGY AND EQUILIBRIUM VALUES FOR THE ACTION OF CARBON AND CARBON MONOXIDE ON SULPHUR TRIOXIDE AT VARIOUS TEMPERATURES

Temperature deg. F.	$SO_3 + \frac{1}{2}C \rightarrow SO_2 + \frac{1}{2}CO_2$			$SO_3 + CO \rightarrow SO_2 + CO_2$		
	ΔF cal. per gram mol. wt.	$\frac{\text{Per cent } SO_3}{\text{Per cent } SO_2}$	Per cent S as SO_3	ΔF cal. per gram mol. wt.	$\frac{\text{Per cent } SO_3}{\text{Per cent } SO_2}$	Per cent S as SO_3
		For 5 per cent CO_2			For $\frac{CO_2}{CO} = 10$	
500	−35 915	4.6×10^{-16}	4.6×10^{-14}	−45 463	2.5×10^{-13}	2.5×10^{-11}
1000	−41 843	1.3×10^{-12}	1.3×10^{-10}	−45 357	6.4×10^{-12}	6.4×10^{-10}
1500	−47 769	6.1×10^{-11}	6.1×10^{-9}	−45 305	8.5×10^{-9}	8.5×10^{-7}
2000	−53 736	6.2×10^{-10}	6.2×10^{-8}	−45 331	6.1×10^{-7}	6.1×10^{-5}
2500	−59 590	2.8×10^{-9}	2.8×10^{-7}	−45 444	9.4×10^{-6}	9.4×10^{-4}

ratio $\frac{\text{per cent } SO_3}{\text{per cent } SO_2}$ that would be obtained if sufficient time were allowed when SO_3 is brought into contact with hot carbon or carbon monoxide. These values, as well as those of the percentage of sulphur present as SO_3, are also shown in Table 34. Since the values of $\frac{\text{per cent } SO_3}{\text{per cent } SO_2}$ depend on the values of CO_2 in the reaction (1), and on the value of the ratio $\frac{\text{per cent } CO_2}{\text{per cent } CO}$ in reaction (2), the data are given for 5 per cent CO_2 and $\frac{\text{per cent } CO_2}{\text{per cent } CO} = 10$, respectively. These conditions are chosen as representative of a reducing zone.

It should be emphasized that the values given in Table 34 do not represent equilibria in the final stack gases but only those in the presence of carbon and carbon monoxide with practically no oxygen. It is realized of course that the gases in a boiler furnace are far removed from any conditions of chemical equilibrium. The fact that the reduction does take place to such a large extent, however, is explained by the theory, and the possibility that further reduction of SO_3 may be brought about by certain changes in the firing is suggested by the data.

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